IMPROVING THE FIDELITY OF CORAL-BASED CLIMATE RECORDS: A ROADMAP FOR BYPASSING INTERCOLONY VARIABILITY AND DIAGENESIS

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IMPROVING THE FIDELITY OF CORAL-BASED CLIMATE RECORDS: A ROADMAP FOR BYPASSING INTERCOLONY VARIABILITY AND DIAGENESIS

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For my parents, Rafiq and Naseem

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

$\delta^{18}O$	**Ratio of oxygen-18 to oxygen-16**
$\delta^{18}O_{sw}$	**Ratio of oxygen-18 to oxygen-16 in seawater**
‰	**Per mil or per thousand**
1σ, 2σ	**One standard deviation, two standard deviations**
μm	**micrometer**
COCs	**Centers of calcification**
ICP-OES	**Inductively coupled plasma – optical emission spectrometer**
ICP-MS	**Inductively coupled plasma – mass spectrometer**
ERSST	**Extended reconstructed sea-surface temperatures**
SEM	**Scanning electron microscope**
SIMS	**Secondary ion mass spectrometer**
Sr/Ca	**Ratio of strontium to calcium**
SSS	**Sea-surface salinity**
SST	**Sea-surface temperature**
mm	**millimeter**
XRD	**X-ray diffraction**

SUMMARY

The tropical oceans are a critical part of climate system, modulating global temperature and precipitation patterns on a variety of timescales. Yet, decadal-to-centennial scale climate variability in the tropics remains poorly characterized due to the dearth of instrumental observations prior to 1970. Massive scleractinian corals are excellent records of past oceanographic variability as they are widely distributed across the tropical oceans, form seasonally-banded skeletons, and can be absolutely dated via U/Th. However, accuracy of coral-based climate reconstructions has been questioned as corals growing on the same reef can produce very different geochemical signals. Diagenetic alteration, which is prevalent among both modern and fossil corals, is also known to significantly compromise the fidelity of coral-based reconstructions. In this thesis, I assess the reproducibility of coral-derived temperature and salinity records using a collection of neighboring corals that grew at Palmyra Atoll between 1980-2010. I also explore the potential of using secondary ion-probe mass spectrometry (SIMS) to extract reliable climate information an altered fossil coral.

Chapter 2 assesses intercolony reproducibility of coral $\delta^{18}O$ and Sr/Ca records using 5 cores from Palmyra Atoll (6˚N, 162˚W). In general, Palmyra coral $\delta^{18}O$ and Sr/Ca records exhibit monthly to interannual variability that is consistent with temperature observations, and reproducible among different colonies. However, the absolute values of individual coral $\delta^{18}O$ and Sr/Ca records are consistently offset from each other. The temperature sensitivity of coral Sr/Ca also varies among different colonies, producing 5 distinct Sr/Ca-SST calibrations. The presence of intercolony variability among Palmyra

corals implies that reconstructions based on individual fossil corals from this site may be unable to resolve mean climate changes smaller than ~1.4˚C. However, multiple overlapping corals can be used to constrain climate-driven differences in mean $\delta^{18}O$ and Sr/Ca between two time periods, providing more reliable estimates of mean climate change.

Chapter 3 presents a comprehensive assessment of the reproducibility of SIMS Sr/Ca measurements, in order to extract a reliable Sr/Ca-based SST record from an altered fossil coral. At micrometer-scales, the coral skeleton is comprised of two basic features: (i) centers of calcification (COCs), which account for <5-8% of the coral skeleton and contain consistently higher Sr/Ca, and (ii) aragonite fibers, which account for >90% of the coral skeleton and are consistently lower in Sr/Ca. The geochemical composition of both these features is highly variable at micrometer-scales, however reliable estimates of bulk Sr/Ca can be readily obtained using SIMS by making 3-4 measurements, per month of skeletal growth, on only the aragonite fibers. With this approach, credible Sr/Ca-based SST records in all modern coral samples where COCs were successfully avoided. Application of this technique to two lightly-altered sections of a young fossil coral reveals that low levels of diagenesis do not impact the fidelity of bulk Sr/Ca measurements. Across a heavily-altered patch on the same fossil coral, where bulk measurements erroneously suggest the ocean was up to ~6˚C cooler, targeted SIMS analyses of only pristine material provides both bulk Sr/Ca estimates and a ~4yr time series that are consistent with SST. Overall, these results demonstrate that SIMS is a powerful tool that can be used to verify the accuracy of reconstructions from fossil corals.

INTRODUCTION

The tropical oceans modulate weather and climate patterns across the globe via atmospheric teleconnections on interannual [e.g. *McPhaden et al.*, 2006] and decadal-centennial [e.g. *Kosaka and Xie*, 2013; *Fyfe et al.*, 2016; *Meehl et al.*, 2016] timescales. Accurate projections of future climate change require a thorough understanding of the dynamics governing tropical climate variability on decadal and longer timescales. Yet, much of these underlying dynamics remain poorly characterize due to the lack of instrumental observations across much of the 20th century [e.g. *Deser et al.*, 2010; *Solomon and Newman*, 2012; *Tokinaga et al.*, 2012b]. For example, the International Comprehensive Ocean-Atmosphere Data Set (ICOADS) which forms the basis for most gridded temperature data products, contains fewer than 5 observations in across the equatorial Pacific for most months between 1900-1970 [*Woodruff et al.*, 1987]. It comes as no surprise then that gridded/interpolated instrumental datasets, which represent our best attempts at filling gaps in the instrumental observations, show inconsistent trends in sea-surface temperature (SST) [*Deser et al.*, 2010] and sea-surface salinity (SSS) [*Tokinaga et al.*, 2012b] across the 20th century.

Massive scleractinian corals are one of the few geologic archives capable of providing monthly-annually resolved, *in situ* records of past oceanic and environmental variability. The aragonitic skeletons of these corals incorporate a wide range of geochemical tracers that can be used to reconstruct oceanic parameters, such as surface temperature [*Weber and Woodhead*, 1972; *Weber*, 1973], surface salinity [e.g. *Ren et al.*, 2003], pH [e.g. *Hönisch et al.*, 2004], and seawater chemistry [e.g. *Gothmann et al.*, 2015].

Recent studies have also explored the use of coral geochemistry to reconstruct wind variability [*Shen et al.*, 1992; *Thompson et al.*, 2015], anthropogenic CO_2 emissions [*Swart et al.*, 2010; *Dassié et al.*, 2013], land use changes [e.g. *Inoue et al.*, 2014], and many other environmental parameters. Massive corals have become ideal tools for investigating tropical climate variability in the more recent past, as they (i) are widely distributed throughout the tropics, (ii) live for several decades to centuries, (iii) continuously precipitate seasonally-banded skeletons at rates of up to 30mm/yr [*Corrège*, 2006], and (iv) can be accurately dated using U/Th [*Edwards et al.*, 1987; *Cobb et al.*, 2003a]. As such, corals can provide continuous, centuries-long, monthly-to-annually resolved records of past climate variability with well-constrained age models [*Corrège*, 2006; *Jones et al.*, 2009; *Lough*, 2010]. Cores extracted from living (hereafter called "modern") corals are now routinely used to supplement and extend instrumental observations across the tropics. Today, a hundred or so such records exist [e.g. *Lough*, 2010], allowing researchers to attempt multiproxy reconstructions of basin-wide and global-ocean changes using mostly coral-derived records [e.g. *McGregor et al.*, 2015; *Tierney et al.*, 2015].

At the forefront of coral paleoclimate research is the use of so-called "fossil" corals to reconstruct climate variability in the more distant past. Interpreting proxies measured in fossil corals, however, presents some key challenges. Unlike records from modern corals, which are usually benchmarked against instrumental data, fossil coral-based reconstructions infer changes in mean climate by comparing coral geochemistry across different corals scattered through time [e.g. *Cobb et al.*, 2003b; *Felis et al.*, 2014a; *Toth et al.*, 2015]. These reconstructions rely on the assumption that neighboring corals from the same reef respond to climate in the exact same way. Yet, it has long been recognized that coral geochemistry varies considerably between neighboring colonies on the same reef [e.g. *Weber and Woodhead*, 1970; 1972; *Weber*, 1973]. This intercolony variability presents a major barrier to reconstructing climate using fossil corals, as there are no clear pathways for determining whether or not differences in geochemical signals among corals reflect actual changes in climate. Diagenetic alteration of coral skeletons is another major concern attempting to reconstruct past climate variability using fossil corals, as few tools exist for assessing the accuracy of these reconstructions. To provide broader context for the research presented in this dissertation, this chapter (i) provides a brief overview of two commonly used coral proxies, oxygen isotope and strontium-to-calcium ratios, and (ii) describes key challenges using applying for fossil corals for climate reconstruction, namely intercolony variability and diagenesis.

1.1 Coral $\delta^{18}O$ – A dual temperature and salinity proxy

Coral skeletons are primarily composed of aragonite, one of the two common calcium carbonate ($CaCO_3$) polymorphs. Similar to many marine carbonates [e.g. *Epstein et al.*, 1951; *Urey et al.*, 1951; *Epstein et al.*, 1953], the ratio at which stable oxygen isotopes ($\delta^{18}O$) are incorporated into coral skeletons is related to both temperature and the oxygen isotopic ratio of seawater ($\delta^{18}O_{sw}$) [*Weber and Woodhead*, 1972]. Variations in seawater $\delta^{18}O$ are strongly coupled with salinity, in that they also echo a balance between precipitation, evaporation, and ocean advection [*Conroy et al.*, 2014; 2017]. As such, coral $\delta^{18}O$ tracks the combined change in both SST and SSS. To date, the vast majority of climate reconstructions using modern and/or fossil corals are based on coral $\delta^{18}O$ measurements [*Lough*, 2010].

While coral $\delta^{18}O$ tracks two very different oceanic parameters, SST and SSS changes in the tropics are tightly coupled on short timescales, amplifying seasonal climate variability recorded by coral $\delta^{18}O$. This covariability arises from the fact that warmer temperatures enhance local convective activity, while cooler temperatures suppress convection. As such, both warmer and fresher conditions drive coral $\delta^{18}O$ towards lighter or more depleted values, whereas cooler temperatures and increased salinity drive coral $\delta^{18}O$ towards heavier values. Thus at research sites far from converging water masses, or complicated ocean circulation patterns [e.g. *Cahyarini et al.*, 2014], coral $\delta^{18}O$ variations are primarily reflect changes in SST.

Coral $\delta^{18}O$ records from "modern", or living, corals have extended instrumental observations well beyond the 20th century at many locations [e.g. *Linsley et al.*, 1994; *Quinn et al.*, 1996; *Druffel and Griffin*, 1999; *Cole*, 2000; *Kuhnert et al.*, 2000; *Hendy*, 2002; *Damassa et al.*, 2006; *Linsley et al.*, 2006; *Quinn et al.*, 2006; *Calvo et al.*, 2007; *Goodkin et al.*, 2008; *Kilbourne et al.*, 2008; *Zinke et al.*, 2014; *Druffel et al.*, 2015]. On decadal-to-centennial timescales, however, differing secular trends in SST and SSS confound the interpretations of long coral $\delta^{18}O$ records. This is evident in coral $\delta^{18}O$ records from central tropical Pacific islands, where trends towards lighter or more depleted $\delta^{18}O$ values across the late-20th century at some sites are not mirrored by an increase in local SST [e.g. *Nurhati et al.*, 2009; 2011a; *Carilli et al.*, 2014]. A growing body of paleoclimate evidence suggests that variability in the East Asian Monsoon [e.g. *Oppo et al.*, 2009; *Tierney et al.*, 2010], migration of the Intertropical Convergence Zone [e.g. *Haug et al.*, 2001; *Sachs et al.*, 2009; *Rustic et al.*, 2015], and/or changes in other large-scale climate features do indeed drive different long-term trends in SST and SSS. As such, an independent SST proxy is needed to separate the contributions of temperature and salinity to coral $\delta^{18}O$ records.

1.2 Coral Sr/Ca – an SST-only proxy

A temperature dependent relationship in the incorporation of strontium relative to calcium (Sr/Ca) in coral skeletons was discovered shortly after the development of coral $\delta^{18}O$ [*Weber*, 1973; *Smith et al.*, 1979]. However, it would take nearly two decades of improvements in analytical instrumentation before cheaper, faster, and more reliable coral Sr/Ca measurements became possible [*Beck et al.*, 1992; *Schrag*, 1999]. Since then, many new trace metal coral proxies (e.g. Mg/Ca, Ba/Ca, U/Ca, Li/Ca, Li/Mg) have been developed to track temperature and other environmental parameters [*Corrège*, 2006; *Sinclair*, 2015].

Of the various metal/Ca proxies now available, coral Sr/Ca ratios across a range of coral species and from many different sites show strong empirical relationships with SST [e.g. *Quinn and Sampson*, 2002; *Corrège*, 2006; *DeLong et al.*, 2011]. Coral Sr/Ca ratios offer a distinct advantage over $\delta^{18}O$, in that seawater Sr/Ca composition is relatively constant on timescales $<10^5$ years [e.g. *Beck et al.*, 1992] and coral Sr/Ca ratios are not influenced by salinity [*Moreau et al.*, 2015]. Coral Sr/Ca provides direct estimates of temperature, calculated by calibrating several years of Sr/Ca measurements from the top of a living coral to local SST, and then applying this calibration to Sr/Ca measurements from the rest of the core. Using this approach, Sr/Ca records modern corals have also used to extend instrumental SST observations well beyond the 20th century [e.g. *Zinke et al.*, 2004; *Linsley et al.*, 2006; *Quinn et al.*, 2006; *Alibert and Kinsley*, 2008; *Goodkin et al.*, 2008; *Zinke et al.*, 2008; *Nurhati et al.*, 2011b; *DeLong et al.*, 2012; *Zinke et al.*, 2015]. Paired measurements of coral Sr/Ca and coral $\delta^{18}O$ can even be used to isolate past variations in $\delta^{18}O_{sw}$ [e.g. *Ren et al.*, 2003; *Cahyarini et al.*, 2008], allowing for more nuanced reconstructions of past climate variability.

1.3 Intercolony variability and the accuracy of fossil coral reconstructions

Since the advent of the coral $\delta^{18}O$ paleothermometer, it has been recognized that the isotopic composition of coral aragonite in not in equilibrium with seawater [*Weber and Woodhead*, 1970; 1972]. Moreover, the degree of "disequilibrium" varies considerably among different species and within individuals of the same species [*Weber and Woodhead*, 1970]. Mean coral $\delta^{18}O$ of *Porites* colonies growing on the same reef can exhibit offsets as large as 0.4‰ [*Linsley et al.*, 1999; *Felis et al.*, 2003; *Cobb et al.*, 2003b; *Stephans et al.*, 2004; *Linsley et al.*, 2008; *Dassié et al.*, 2014], equivalent a temperature difference of ~ 2˚C.

As coral $\delta^{18}O$ tracks the combined change in temperature and salinity, the lack of *in situ* salinity measurements makes it difficult to isolate the sensitivity of coral $\delta^{18}O$ to each parameter. A survey of published coral $\delta^{18}O$ records from across the tropics by *Grottoli and Eakin*, 2007 finds that the relationship between *Porites* coral $\delta^{18}O$ and local SST ranges from -0.16 to -0.47‰ ˚C^{-1}. Spatiotemporal variability in $\delta^{18}O_{sw}$ likely contributes to these discrepancies, however, $\delta^{18}O_{sw}$ across a reef should be minimal enough that regressing coral $\delta^{18}O$ measurements onto local SST would produce similar slopes for corals growing on the same reef. Yet, studies find a similar range of coral $\delta^{18}O$-SST relationships among *Porites* corals growing on the same reef [e.g. *Linsley et al.*, 1999].

Intercolony variability is also observed in coral Sr/Ca, where mean offsets among *Porites* corals can be as high as 0.14mmol/mol or ~2˚C [*de Villiers et al.*, 1995b; *Felis et al.*, 2004; *Linsley et al.*, 2006; *Cahyarini et al.*, 2008; *Pfeiffer et al.*, 2008; *Saenger et al.*, 2008; *Abram et al.*, 2009; *DeLong et al.*, 2011]. Coral Sr/Ca-SST calibrations vary considerably between sites, with slopes ranging from ranging from -0.04 to -0.11mmol mol^{-1} $˚C^{-1}$ [*Corrège*, 2006; *Sinclair*, 2015]. Similar variability in Sr/Ca-SST calibration slopes (-0.03 to -0.09mmol mol^{-1} $˚C^{-1}$) are also observed among neighboring corals from the reef [*Alibert and McCulloch*, 1997; *Saenger et al.*, 2008; *Alpert et al.*, 2016; *DeCarlo et al.*, 2016]. This intercolony variability is particularly problematic for fossil coral Sr/Ca records, which are converted temperature estimates using a Sr/Ca-SST calibration derived for a different colony. With no clear way of knowing which calibration to apply, fossil corals may over/underestimate SST by ±5˚C [e.g. *Corrège*, 2006; *Sinclair*, 2015]. This severely limits the use of fossil corals for reconstructing past climate variability in the tropics, where changes in SST variability is expected to be within 1-2˚C across recent millennia [e.g. *Oppo et al.*, 2009; *Rustic et al.*, 2015] or 3-4˚C across the last glacial-interglacial transition [e.g. *Visser et al.*, 2003; *Koutavas and Joanides*, 2012].

1.4 Potential sources of intercolony variability

A number of explanations for intercolony variability have emerged over the years. A commonly invoked explanation is that growth or skeletal extension rates influence isotopic [e.g. *de Villiers et al.*, 1995a; *Allison*, 1996b; *Cohen and McConnaughey*, 2003; *Felis et al.*, 2003; *Maier et al.*, 2004] and/or trace metal [e.g. *Cohen and Hart*, 2004; *Maier et al.*, 2004; *Goodkin et al.*, 2005; 2007] incorporation into coral skeletons. Corrections for “growth-related” effects have even been applied to coral proxy records [e.g. *Maier et al.*, 2004] to varying degrees of success. Yet, just as many studies demonstrate that extension rates have no discernible impact on coral geochemistry [e.g. *Smith et al.*, 1979; *Alibert and McCulloch*, 1997; *Allison and Finch*, 2004; *Hayashi et al.*, 2013; *Hirabayashi et al.*, 2013].

Similarly tenuous links also exist between intercolony variability and environmental factors such as light [e.g. *Rosenfeld et al.*, 2003; *Reynaud et al.*, 2004; *Juillet-Leclerc and Reynaud*, 2010; *Juillet-Leclerc et al.*, 2014], seawater composition [e.g. *de Villiers*, 1999], local temperature variability [e.g. *Alpert et al.*, 2016], and pH [*Rollion-Bard et al.*, 2003b; *Cole et al.*, 2016], and/or physiological factors such as symbiont activity [e.g. *Cohen*, 2002] and coral gender [e.g. *Carricart-Ganivet et al.*, 2013]. Teasing out how factors these impact coral biomineralization is incredibly important. However, it is worth noting there is often very little information available about a fossil coral's growth environment. Even narrowing down the exact species identification of a fossil coral is often difficult. While modern coral records can be improved by correcting for environmental or physiological factors, there is no objective way of applying these corrections to fossil corals.

Intercolony variability is observed among corals grown in closely-regulated tanks [*Suzuki et al.*, 2005; *Inoue et al.*, 2007; *Hayashi et al.*, 2013], implying that such variability likely arises from the biomineralization process itself. While both coral $\delta^{18}O$ and Sr/Ca are strongly related to temperature, the exact mechanisms controlling the incorporation of isotopes and trace elements into the coral skeleton are poorly understood [*Gagnon et al.*, 2012; *Sinclair*, 2015]. In fact, there is still very little consensus on the mechanisms behind coral biomineralization. Proposed biomineralization frameworks range from biologically-induced models, where skeletal formation is a physicochemical process, to biologicallycontrolled models, where skeletal formation is highly controlled using an organic matrix [*Allemand et al.*, 2011].

Even with multiple lines of evidence lend support to a range of biomineralization frameworks [e.g. *Euw et al.*, 2017], geochemists have primarily focused on a biologically-induced model. In the physicochemical model [*McConnaughey*, 1989a; 1989b; *Cohen and McConnaughey*, 2003], the calcifying fluid is derived from seawater [e.g. *Gagnon et al.*, 2012] and then modified by metabolic processes [e.g. *Gaetani and Cohen*, 2006; *Sinclair*, 2015] to induce the precipitation of aragonite. Within this framework, which is extensively supported by geochemical modeling studies [e.g. *Sinclair*, 2005; *Gaetani and Cohen*, 2006; *Sinclair and Risk*, 2006], aragonite precipitation experiments [e.g. *Gaetani and Cohen*, 2006; *Holcomb et al.*, 2009; *Gabitov et al.*, 2014; *DeCarlo et al.*, 2016], and microscale analyses [e.g. *Cohen et al.*, 2006; *Gagnon et al.*, 2007; 2012], the incorporation of trace metals is controlled by both temperature-dependent partitioning, and varying degrees of Rayleigh fractionation within each new batch of calcifying fluid. These models also support the varying "disequilibrium effects" observed in coral $\delta^{18}O$ [e.g. *Adkins et al.*, 2003].

1.4 Diagenesis

Diagenetic alteration is pervasive in corals, impacting both young modern coral [e.g. *Enmar et al.*, 2000; *Lazar et al.*, 2004; *Quinn and Taylor*, 2006; *Nothdurft and Webb*, 2008; *Nurhati et al.*, 2011a] and older fossil corals [e.g. *Bar-Matthews et al.*, 1993; *Sherman et al.*, 1999; *McGregor and Gagan*, 2003; *Allison et al.*, 2007] alike. Diagenesis manifests as either dissolution and/or precipitation secondary cements (e.g. aragonite, calcite, brucite) along the outer walls of the coral skeleton [e.g. *Nothdurft and Webb*, 2008;

Rabier et al., 2008]. The impacts of dissolution have not been extensively studied [e.g. *Hendy et al.*, 2007], however the impacts of commonly occurring secondary cements on coral $\delta^{18}O$ and Sr/Ca records are well characterized. Secondary aragonite forms while a coral is still submerged in seawater, and as such, is observed in fairly young modern corals [e.g. *Sayani et al.*, 2011]. Secondary aragonite crystals are significantly higher in $\delta^{18}O$ and Sr/Ca than coral aragonite. The inclusion of even 2% of secondary aragonite in powders used for conventional $\delta^{18}O$ and Sr/Ca measurements will produce artifacts of -0.6˚C to -1˚C in temperature reconstructions [e.g. *Allison et al.*, 2007; *Sayani et al.*, 2011].

Secondary calcite cements can occasionally form while a coral is submerged [e.g. *Buster and Holmes*, 2006; *Nothdurft et al.*, 2007], but are more commonly observed in fossil corals that have been exposed to rainwater. The impact of secondary calcite on coral $\delta^{18}O$ and Sr/Ca largely depends on how the calcite crystals are formed. Where dissolution and recrystallization occur simultaneously, secondary calcite cements preserve the original skeletal structure and will have Sr/Ca compositions similar to the original coral skeleton [e.g. *Rabier et al.*, 2008]. However, if this concomitant dissolution and recrystallization occurs across a large enough area, then much of the climate signal recorded within the original coral skeleton could be overwritten. Large calcite crystals that precipitate within skeletal pore spaces have significantly lower $\delta^{18}O$ and Sr/Ca than coral aragonite [e.g. *McGregor and Gagan*, 2003]. The inclusion of even 2% of these secondary calcite cements in powders used for conventional $\delta^{18}O$ and Sr/Ca will produce artifacts as large as +2˚C in temperature reconstructions [e.g. *Allison et al.*, 2007; *Sayani et al.*, 2011].

Fossil corals are now routinely screened for diagenesis using x-ray diffraction (XRD) to confirm the presence of secondary calcite, and either thin-sections or scanning electron microscopy (SEM) to check for secondary aragonite. As all three methods are destructive, diagenesis screening is often conducted some distance away from transects used for coral $\delta^{18}O$ and Sr/Ca measurements. This can be problematic as observations from both modern and fossil corals show that diagenesis levels vary significantly on millimeter-scales [e.g. *Bar-Matthews et al.*, 1993; *Hendy et al.*, 2007; *Hathorne et al.*, 2011]. As such, even with the most through screening procedures, small pockets of diagenesis may go unnoticed, producing significant errors in coral-based climate records.

1.5 Summary

Modern corals have proven to be incredibly versatile archives of climate and environmental variability across recent centuries. Similar reconstructions using fossil corals, however, may be hampered by intercolony variability and diagenesis. This dissertation seeks to provide a roadmap for more accurate fossil-coral based reconstructions. Chapter 2 provides a thorough assessment of intercolony variability in for Palmyra Atoll (6˚N, 162˚W), quantifying potential errors in future paleoclimate reconstructions from this site. As almost all fossil corals contain some degree of diagenetic alteration, Chapter 3 explores the potential of using targeted Sr/Ca analyses via secondary ion mass spectrometry (SIMS) to verify the accuracy of bulk Sr/Ca measurements.

CHAPTER 2. INTERCOLONY VARIABILITY AMONG CORALS AT PALMYRA ATOLL: TOWARDS ROBUST CORAL-BASED ESTIMATES OF MEAN CLIMATE CHANGE

2.1 Abstract

Quantitative estimates of natural climate variability in the tropics are needed to identify anthropogenic climate trends, however instrumental records from this region of the world are relatively short and sparse. Monthly-to-annual oxygen isotopic ($\delta^{18}O$) and strontium to calcium (Sr/Ca) ratios in reef-building corals faithfully track regional climate variability, providing much needed insight into past sea-surface temperature (SST) and salinity changes. However, *Porites* corals growing on the same reef can yield Sr/Ca and $\delta^{18}O$ records with significantly different mean values, making it difficult to accurately combine or compare records. These intercolony offsets equate to uncertainties of 1-3˚C when converted to absolute SST, and hamper the accuracy of mean temperature reconstructions based on the geochemical records based on collection of individual coral colonies. To quantify intercolony variability at Palmyra Atoll, where extensive fossil coral $\delta^{18}O$ records have been previously published, we replicate Sr/Ca and $\delta^{18}O$ measurements across five neighboring corals from this site that grew between 1980-2010. While monthly to interannual variability in Sr/Ca and $\delta^{18}O$ is largely consistent between cores, we document intercolony offsets in mean Sr/Ca of ±0.09mmol/mol (1σ) or ~1˚C, and in $\delta^{18}O$ of ±0.04‰ or ~0.2˚C. We also find that Sr/Ca-SST calibration slopes differ significantly between cores, ranging from -0.06 to -0.12 mmol mol-1 °C-1. Taken together, intercolony variability contributes uncertainties of ±1.4˚C (1σ) to Sr/Ca-based SST reconstructions.

Replicating Sr/Ca records across multiple overlapping corals can greatly reduce these uncertainties. A composite record built using five modern cores, for example, offers a reduced error of ±0.6˚C (1σ).

2.2 Introduction

Improving the accuracy of decadal to centennial climate projections depends requires accurate estimates of natural climate variability on these timescales. However, in the tropical Pacific, where sea-surface temperature (SST) variations profoundly influence global temperature and rainfall patterns on both interannual [*McPhaden et al.*, 2006] and decadal-to-centennial timescales [*Kosaka and Xie*, 2013; *Fyfe et al.*, 2016; *Meehl et al.*, 2016], the quantity of instrumental climate data decreases significantly prior to 1950 [*Deser et al.*, 2010; *Solomon and Newman*, 2012; *Tokinaga et al.*, 2012a], and is virtually nonexistent prior to 1900 [*Woodruff et al.*, 1987]. Paleoclimate reconstructions of tropical Pacific temperature over the last several centuries effectively extend the instrumental record of climate, allowing for the quantification of temperature variations on interannual to centennial timescales of interest [e.g. *Mann et al.*, 2009; *Evans et al.*, 2010; *Wilson et al.*, 2010; *Emile-Geay et al.*, 2013; *McGregor et al.*, 2015; *Tierney et al.*, 2015; *Abram et al.*, 2016].

Long-lived, fast-growing, massive corals of the genus Porites constitute the majority of the sea-surface temperature reconstructions from the tropical Pacific, as they afford monthly-resolved records that can span several centuries. Of these reconstructions, coral oxygen isotopic ($\delta^{18}O$) records are most common, reflecting combined variations in sea-surface temperature (SST) and seawater oxygen isotopes ($\delta^{18}O_{sw}$) [*Epstein et al.*, 1953;

Weber and Woodhead, 1972; *Corrège*, 2006 and references therein]. In the equatorial Pacific, $\delta^{18}O_{sw}$ variations are strongly correlated to sea-surface salinity (SSS) variations, as both variables are governed by evaporation, precipitation, and ocean advection [*Hasson et al.*, 2013; *Conroy et al.*, 2014; 2017]. Given that warm SSTs are closely associated with increased rainfall from enhanced convection, at least on interannual timescales, many studies use coral $\delta^{18}O$ records to reconstruct El Niño/Southern Oscillation (ENSO) variability across recent centuries [e.g. *Cobb et al.*, 2001; *Hereid et al.*, 2012; *Druffel et al.*, 2015] and millennia [*Cobb et al.*, 2003b; 2013; *McGregor et al.*, 2013]. On decadal and longer time-scales, secular trends in tropical SST and hydrology may be largely independent [e.g. *Oppo et al.*, 2009; *Sachs et al.*, 2009; *Tierney et al.*, 2010; *Rustic et al.*, 2015], requiring the application of an independent SST proxy to distinguish between the temperature and salinity contributions to coral $\delta^{18}O$ records.

Extensive empirical data underscore the utility of coral Sr/Ca ratios as a robust proxy for ocean temperature [*Weber*, 1973; *Smith et al.*, 1979; *Beck et al.*, 1992; *Quinn and Sampson*, 2002; *Inoue et al.*, 2007; *DeLong et al.*, 2013; *Sinclair*, 2015; *Kuffner et al.*, 2017], even though a complete mechanistic framework for temperature-dependent incorporation of Sr into coral skeletal aragonite remains elusive [*Gaetani and Cohen*, 2006; *Sinclair et al.*, 2006; *Allison et al.*, 2011; *Gagnon et al.*, 2012]. Coral Sr/Ca's utility as a temperature proxy stems from the fact that both Sr and Ca are conservative in seawater on timescales shorter than 105yrs [*Beck et al.*, 1992; *Gothmann et al.*, 2015], as such, coral Sr/Ca is unaffected by changes in salinity [*Moreau et al.*, 2015]. Dozens of coral Sr/Ca-based temperature records now exist throughout the tropics, supplementing and extending the instrumental SST record in many data-sparse regions [e.g. *Alibert and McCulloch*, 1997; *DeLong et al.*, 2007; *Nurhati et al.*, 2009; 2011a; *DeLong et al.*, 2012; *Maupin et al.*, 2014; *Linsley et al.*, 2015; *Thompson et al.*, 2015].

Paired measurements of coral Sr/Ca and coral δ18O allow for the quantification of both SST and $\delta^{18}O_{sw}$ variations in the past [e.g. *Ren et al.*, 2003; *Cahyarini et al.*, 2008]. While relatively rare, such paired records afford a more complete understanding of natural vs anthropogenic temperature and/or hydrological changes across the tropics [e.g. *Felis et al.*, 2009; *Nurhati et al.*, 2009; *Hetzinger et al.*, 2010; *Nurhati et al.*, 2011a; *Carilli et al.*, 2014; *Toth et al.*, 2015]. Nonetheless, using either coral Sr/Ca or $\delta^{18}O$ to investigate past climate changes poses a number of challenges, which we review in the following paragraphs.

Several studies that examine multiple coral $\delta^{18}O$ and Sr/Ca records from the same reef uncover a wide range of absolute $\delta^{18}O$ and Sr/Ca values that cannot be explained by small-scale physical and/or geochemical variations on the reef. While not relevant to the reconstruction of climate variations from single, long coral cores (which constitute the vast majority of coral paleoclimate reconstructions), such "intercolony offsets" present a significant obstacle to quantitative reconstructions of past climate states from individual sub-fossil (hereafter "fossil") corals. These intercolony offsets can be as large as 0.4‰ in coral $\delta^{18}O$ [*Felis et al.*, 2003; *Cobb et al.*, 2003b; *Stephans et al.*, 2004; *Linsley et al.*, 2008; *Dassié et al.*, 2014], equivalent to 2˚C in $\delta^{18}O$-derived SST [*Epstein et al.*, 1953], and up to 0.14mmol/mol in coral Sr/Ca [*de Villiers et al.*, 1995b; *Felis et al.*, 2004; *Linsley et al.*, 2006; *Cahyarini et al.*, 2008; *Pfeiffer et al.*, 2008; *Saenger et al.*, 2008; *Abram et al.*, 2009; *DeLong et al.*, 2011], equivalent to ~2˚C in Sr/Ca-derived SST [*Corrège*, 2006]. Intercolony offsets as large as 0.4‰ in coral $\delta^{18}O$ and 0.05mmol/mol in Sr/Ca are also observed among corals grown in closely-regulated tanks [*Suzuki et al.*, 2005; *Inoue et al.*, 2007; *Hayashi et al.*, 2013], suggesting that non-environmental factors, commonly dubbed "vital effects", may influence mean coral $\delta^{18}O$ and Sr/Ca values recorded by a colony. At this point, it is unclear whether such inter-colony offsets differ from site to site or, more likely, represent an intrinsic feature of coral colonies that remain poorly characterized by available studies.

The sensitivity of coral Sr/Ca to SST changes varies across corals collected at the same site, and across corals collected at different sites. Discrepancies in empirical Sr/Ca-SST calibrations for Porites corals growing at different sites were noted early on [*Alibert and McCulloch*, 1997], with published Sr/Ca-SST slopes ranging from -0.04 to -0.12mmol mol^{-1} $^{\circ}C^{-1}$, with an average of 0.06mmol mol^{-1} $^{\circ}C^{-1}$ [*Corrège*, 2006; *Sinclair*, 2015]. The lack standardization of coral Sr/Ca measurements across laboratories [*Hathorne et al.*, 2013a] and differences in how calibrations are constructed [*Corrège*, 2006 and references there in] could explain some of this discrepancy in Sr/Ca-SST sensitivity. Yet, subsequent studies examining corals at the same site uncovered a similar range (-0.03 to 0.09mmol mol^{-1} $^{\circ}C^{-1}$) of Sr/Ca-SST slopes [*Alibert and McCulloch*, 1997; *Saenger et al.*, 2008; *Alpert et al.*, 2016; *DeCarlo et al.*, 2016]. The sensitivity of coral $\delta^{18}O$ to SST in Porites corals also varies from -0.16 to -0.47‰ $^{\circ}C^{-1}$ between sites, largely due to differing contributions of seawater $\delta^{18}O$ [*Grottoli and Eakin*, 2007]. For corals growing at the same site, coral $\delta^{18}O$-SST slopes vary between -0.23 to 0.53‰ $^{\circ}C^{-1}$ [e.g. *Linsley et al.*, 1999; *Stephans et al.*, 2004]. Intercepts for both coral $\delta^{18}O$-SST and Sr/Ca-SST equations also vary, reflecting intercolony offsets in both coral proxies as noted in the previous paragraph.

Intercolony variability, whether in the form of systematic offsets and/or differences in proxy-SST sensitivity, represents a significant hurdle for paleoclimate reconstructions based on fossil corals, which by definition requires comparing geochemical signals across multiple coral colonies [*Tudhope*, 2001; *Cobb et al.*, 2003b; *Corrège et al.*, 2004; *Felis et al.*, 2004; *DeLong et al.*, 2010; *Cobb et al.*, 2013; *Felis et al.*, 2014b; *Toth et al.*, 2015]. In such cases, intercolony offsets can far exceed the magnitude of temperature-related changes in coral geochemistry across the Holocene, when decadal-to-centennial changes in tropical SST likely did not exceed 1-2˚C [e.g. *Visser et al.*, 2003; *Oppo et al.*, 2009; *Koutavas and Joanides*, 2012]. A potential strategy for pursuing climate reconstructions using such material involves generating Sr/Ca and $\delta^{18}O$ records across multiple corals the grew during target time periods [e.g. *Hendy*, 2002]. Such ensembles of sub-fossil (hereafter "fossil") coral records can then be quantitatively compared to similar ensembles from modern coral corals, yielding accurate estimates of absolute temperature change. To date, very few such modern coral ensembles exist, even at sites where a large number of fossil coral climate reconstructions exist.

Here, we use five overlapping coral cores recovered from Palmyra Atoll (5°53'N, 162°5'W) to assess inter-colony differences in coral Sr/Ca and $\delta^{18}O$, and their relationship to instrumental SST, over the period 1980 to 2010. We use these data to provide quantitative estimates of the uncertainties associated with Sr/Ca-based and $\delta^{18}O$-based SST reconstructions from both single-colony reconstructions as well as from multiple fossil coral reconstructions [e.g. *Cobb et al.*, 2003b]. We also assess the potential impact of intercolony Sr/Ca and $\delta^{18}O$ variability on coral-based $\delta^{18}O_{sw}$ reconstructions from Palmyra Atoll. We discuss the implications of our coral reproducibility study for the design of future coral reconstruction projects and multi-proxy synthesis studies that employ coral reconstructions.

2.3 Methods

We present new data from a total of four coral cores recovered from live *Porites* (*sp.*) colonies growing on the western and southern reef terraces of Palmyra Atoll (5°53'N, 162°5'W) in the central tropical Pacific (Figure 2-1; Table 2-1). Cores PM1 and PM5 were collected in May 1998 from two colonies growing <100m apart, and ~10m deep, near the center of Palmyra's western reef terrace by K.M. Cobb. Core P13 was collected in June 2007 by E.R.M. Druffel from a colony growing at a depth of 35m on the atoll's southern reef. Core PAL2 was collected in June 2010 by NOAA Coral Reef Ecosystem Program (CREP) from a colony growing at a depth of 12.5m near the lagoon channel. A subset of coral Sr/Ca from PAL2 is presented in *DeCarlo et al.*, 2016, but we reanalyzed and extended this coral Sr/Ca record from this core employing the same method used for all the Sr/Ca measurements presented here, to ensure uniformity across our coral datasets. The fifth core, hereafter referred to as PM, has previously published $\delta^{18}O$ [*Cobb et al.*, 2001] and Sr/Ca [*Nurhati et al.*, 2009; 2011a] records from a 112-yr-long core recovered in May 1998 by K.M. Cobb.

Table 2-1: Location and extension rates of cores used in this study.

Core	Location	Extension Rate (mm/yr)
PM	5° 52' 41"N, 162° 8' 30"W	19.0 ± 0.9
PM1	5° 52' 41"N, 162° 8' 30"W	16.2 ± 0.7
PM5	5° 52' 41"N, 162° 8' 30"W	15.8 ± 1
P13	5° 52' 12"N, 162° 8' 9.6"W	16.9 ± 0.6
PAL2	5° 51' 57.6"N, 162° 6' 36"W	6 ± 1

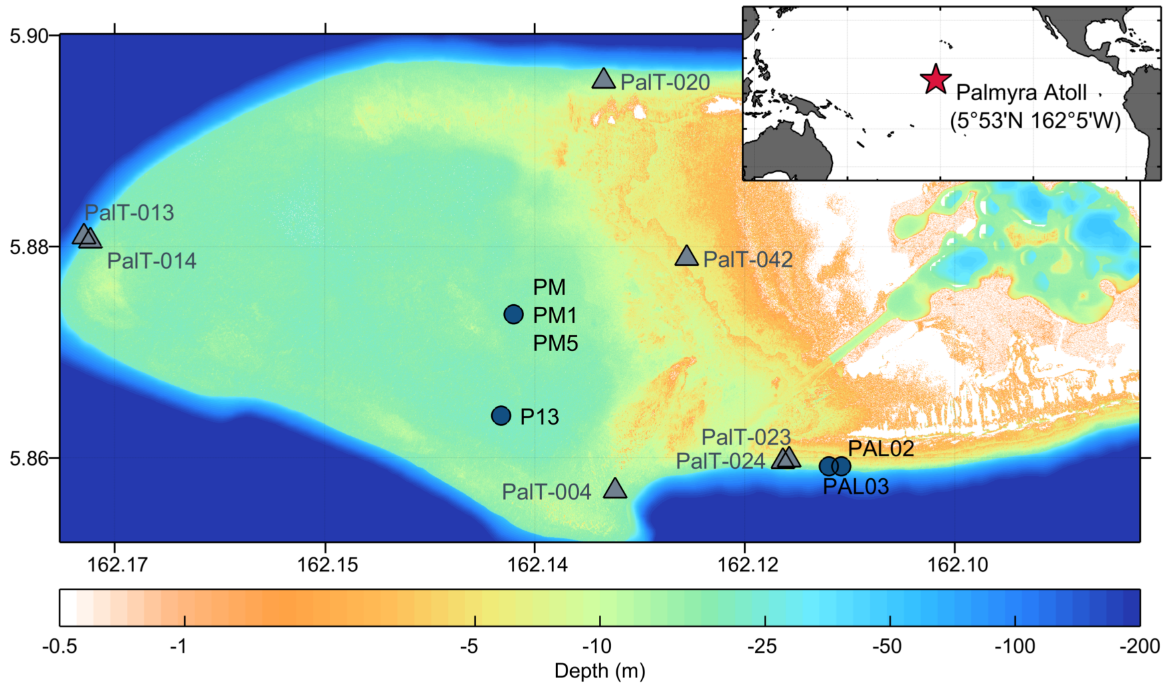

Figure 2-1: Locations of *Porites* colonies (blue circles) and *in situ* temperature loggers (grey triangles) at Palmyra Atoll. Logger data is provided by NOAA Coral Reef Ecosystem Program.

The preparation of the cores for geochemical analysis and SEM imaging followed standard procedures. First, cores were cut into ~5-10mm thick longitudinal slabs to reveal the growth axes and subsequently sonicated and rinsed in deionized water. The coral slabs were x-rayed at the Stamps Health Services at Georgia Tech to reveal the underlying skeletal architecture. Optimal sampling transects were selected close to the coral's primary growth axis, while taking care to avoid problematic areas of the core such as steeply angled corallites (oblique to the surface of the slab), merging corallite fans, and/or disorganized corallites, which have been shown to significantly bias coral $\delta^{18}O$ and Sr/Ca values [*Alibert and McCulloch*, 1997; *Cohen and Hart*, 1997; *DeLong et al.*, 2013]. Corals were screened for diagenetic alteration using either a Hitachi S-800 field emission gun scanning electron microscope (SEM) or a LEO 1530 thermally-assisted field emission SEM using procedures outlined in *Sayani et al.*, 2011.

Coral Sr/Ca ratios were measured using a Horiba Jobin-Yvon Ultima 2C Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) located at Georgia Tech. Samples for ICP-OES analysis were prepared by milling 150-200μg of coral powder at 1mm intervals along a transect parallel to the primary growth axis, and then digesting in 2-2.7mL of 2% trace-metal grade HNO_3 to obtain Ca concentrations of 30ppm. Analytical precisions of < ±0.1% or ±0.01mmol/mol (1σ) are routinely obtained by bracketing each sample with an internal standard and applying a nearest-neighbor correction [*Schrag*, 1999]. Repeat measurements of an in-house coral-based standard, measured 3-5 times per run, allow for the quantification of long-term instrumental drift. Coral Sr/Ca presented here are not corrected to JCp-1 [*Hathorne et al.*, 2013a], however repeated analyses of this standard over time yield a Sr/Ca value of 8.99±0.01mmol/mol (n=25).

Coral $\delta^{18}O$ ratios were measured using either a Thermo Scientific Delta V or a Thermo MAT 253 isotope ratio mass spectrometer located at Georgia Tech, both equipped with Finnigan Kiel IV carbonate devices. Samples are prepared by milling 60-100μg of coral power at 1mm intervals along the same transects used for Sr/Ca measurements. Analytical precision based on repeated analyses of a homogenized aragonite standard is estimated to be < ±0.07‰ (1σ) for $\delta^{18}O$ and ±0.05‰ (1σ) for $\delta^{13}C$ on both the Delta V and the MAT 253. For each run of coral powders, a powdered coral standard of known isotopic composition was analyzed 8-10 times during a single run to monitor precision as well as long-term drift.

Age models for each coral Sr/Ca record were constructed by identifying annual cycles across a number of 1mm-spaced analyses, guided by well-established extension rates for *Porites* corals growing at Palmyra Atoll (12-20mm/yr) [*Cobb*, 2002]. As coral Sr/Ca is inversely correlated with SST, we assigned the highest (lowest) Sr/Ca values a calendar date of February 1st (September 1st), corresponding to peak winter (summer) temperatures, respectively, in the ERRST3b monthly climatology [*Cobb et al.*, 2001]. Ages of samples between winter and summer tie points were linearly interpolated. A manual check of the resulting age model against sub-seasonal features reflected in both coral Sr/Ca and ERSSTv3b time series resulted in small corrections of 1-2 months for a subset of the data to obtain a final chronology. Extension rates for cores PM, PM1, PM5, and P13, estimated by counting the number of 1mm Sr/Ca data points per year, and range from 10-28mm/yr in any given year. The annual extension rate for cores PM, PM1, PM5, and P13, averaged across the interval analyzed on each core, are 19, 16, 16, and 17 mm/yr respectively. In contrast, extension rates for core PAL2 were significantly smaller, ranging from 5 to 8mm each year, averaging 6mm/yr between 2002-2010. Monthly coral Sr/Ca records presented here are each ~8-18yrs in length, and span 1980-2010 with multiple overlapping intervals. Initial age models for new $\delta^{18}O$ records from cores PM1 and PM5, re-measured along the same transects used for coral Sr/Ca records, are based on the final Sr/Ca-derived chronologies for cores. To account for human error during resampling, final age models for each coral $\delta^{18}O$ record were obtained by manually checking each record with ERSSTv3b which resulting in maximum shifts of 1-2 months for any given point.

We use the following instrumental datasets in this study: (i) *in situ* Palmyra SST data from 2000-2002 from *Nurhati et al.*, 2009, and from 2004-2006 and 2008-2012 from

NOAA CREP, (ii) gridded temperatures from the ERSSTv3b grid box (6˚N,-162˚E) containing Palmyra [*Smith et al.*, 2008], and (iii) gridded surface salinity from *Delcroix et al.*, 2011, from the (6˚N,198˚E) grid box.

2.4 Results

2.4.1 Reproducibility among coral Sr/Ca records

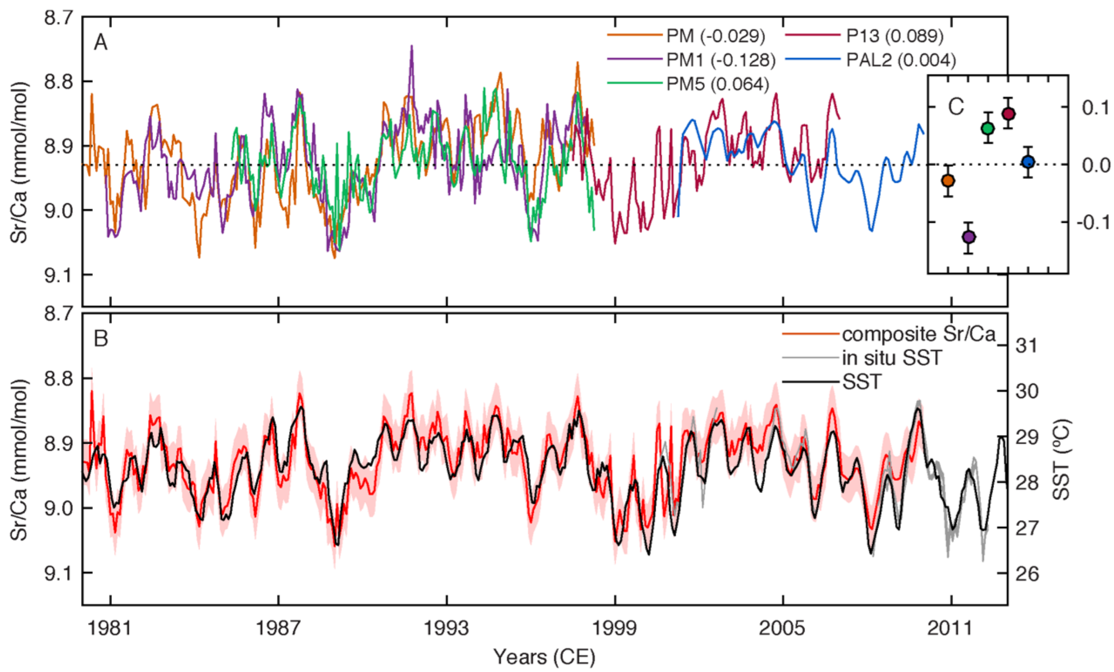

Figure 2-2: (A) Monthly Sr/Ca records, with offsets removed, from cores PM (orange) [Nurhati et al., 2009, 2011], PM1 (purple), PM5 (green), P13 (red), and bimonthly Sr/Ca from PAL2 (blue). (B) Composite modern coral Sr/Ca, computed using records in panel A, compared to both in situ SST (grey) and ERSSTv3b (black) [Smith et al., 2008]. Red shading represents analytical uncertainty compounded with intercolony Sr/Ca variability scaled by the number of cores in the composite. (C) Offsets in mean Sr/Ca values of each record shown in panel A. Error bars (3σ) represent analytical precision of measurements in each record.

Between 1985-1998, overlapping monthly coral Sr/Ca time series from PM, PM1, and PM5 are well correlated with each other (R=0.56 to 0.59, P<0.05; Figure 2-2A). Likewise, between 1997-2007, bimonthly coral Sr/Ca from core P13 and PAL2 are well correlated with each other ($R=0.53$, $P<0.05$; Figure 2-2A). Not surprisingly, smoothing each time series by 3-months or more [e.g. *Allison and Finch*, 2004], substantially improves correlations among the different colonies, as it minimizes the contributions of analytical and chronological uncertainties to each record [*DeLong et al.*, 2013] . Coral Sr/Ca records from cores PM, PM1, PM5, and PAL2 are well correlated with ERSSTv3b ($R=-0.72$ to -0.80, $P<0.05$). Between 1997-2007, coral Sr/Ca from core P13 is highly correlated with ERSST ($R=-0.77$). However prior to 1997, P13's coral Sr/Ca record diverges considerably from SST and overlapping Sr/Ca from cores PM, PM1, and PM5 (Figure A1-A). SEM screening shows no evidence of diagenesis in core P13 between 1997-2007, however from down-core from 1997, we observe considerable secondary aragonite infilling. As such, we only use the unaltered portion of P13 in this study.

The amplitudes of seasonal cycles in coral Sr/Ca are largely consistent among the five cores across periods where they overlap (Table 2-2). Between 1985 – 1998, cores PM, PM1, and PM5 exhibit statistically indistinguishable seasonal amplitudes of 0.057±0.016, 0.063±0.019, and 0.058±0.013mmol/mol respectively (Figure 2-3). Between 2002-2010, P13 and PAL2 display similar seasonal amplitudes of 0.062±0.021mmol/mol and 0.054±0.025mmol/mol (Figure 2-3).

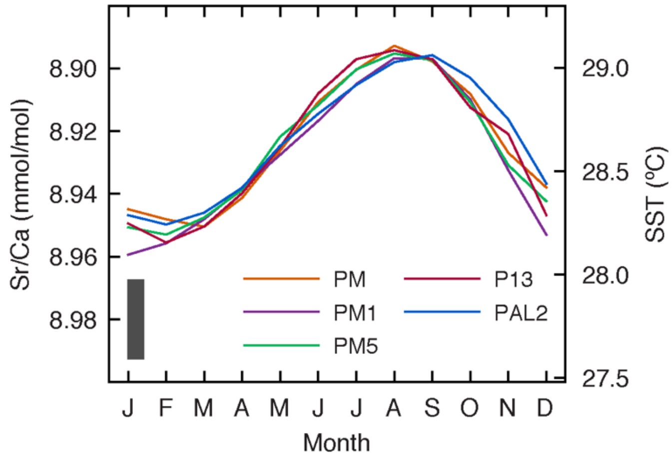

Figure 2-3: Seasonal amplitudes of coral Sr/Ca in cores PM (orange), PM1 (purple), PM5 (green), P13 (red), and PAL2, (blue). Grey bar represents the average error (±1σ) in mean Sr/Ca values for each month.

As with monthly and seasonal variability, interannual variability is also largely consistent among the different cores and SST over their respective overlaps (Table 2-2). Interannual coral Sr/Ca variability was isolated by removing the seasonal cycle and applying a 13-month running mean filter to each record (Figure 2-4A), approximating a ~2yr low-pass filter (Figure 2-4B). Interannual variability is estimated by computing the standard deviation of each filtered record. Cores PM and PM1 exhibit similar interannual variability (±0.043mmol/mol; 1σ) between 1985-1998, whereas core PM5 exhibits somewhat muted interannual variations (±0.030mmol/mol; 1σ) across this interval (Figure 2-4A). Cores P13 and PAL2 exhibit much lower interannual variability (±0.014 and ±0.016 mmol/mol, 1σ, respectively) between 2002-2006, consistent with weaker ENSO activity in the early 2000s. Interannual coral Sr/Ca records are well-correlated with interannual SST ($R=0.79$ to 0.96; $P<0.05$).

By removing the offsets and then averaging all five records together, we create a composite coral Sr/Ca record that tracks SST better than any of the individual Sr/Ca record across all of the timescales discussed above. On monthly time-scales, the coral Sr/Ca composite is better correlated with SST (R=0.82) than any individual Sr/Ca record (Figure 2-2B). On interannual timescales, the composite coral Sr/Ca is also well correlated with 2-yr lowpass filtered SST (R=-0.89, P<0.05; Figure 2-4B). More importantly, unlike the individual Sr/Ca records, the composite coral Sr/Ca record fully captures all ENSO events between 1985 – 2010.

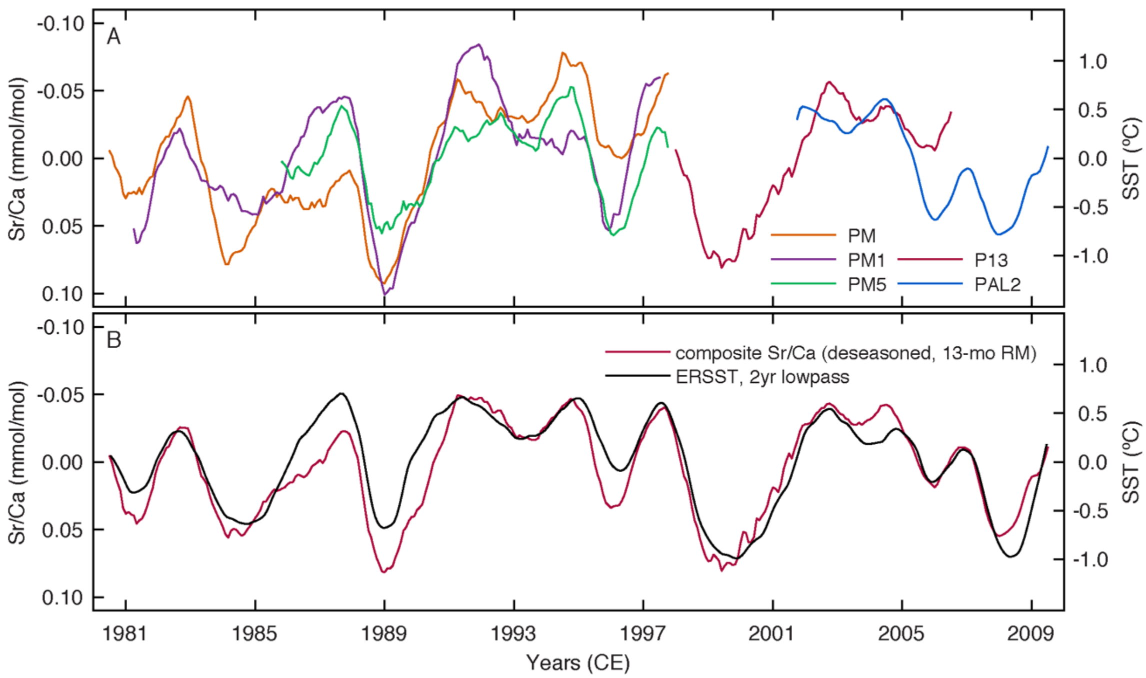

Figure 2-4: Interannual Sr/Ca variability in (A) cores PM (orange), PM1 (purple), PM5 (green), P13 (red), and PAL2 (blue) estimated by removing seasonal cycles from monthly Sr/Ca and applying a 13-month running mean filter. (B) Interannual variability in the coral Sr/Ca composite (red), derived using the same approach for records in panel A, compared with both 2-yr low-pass filtered ERSSTv3b (black).

Despite exhibiting similar variability, the coral Sr/Ca records are systematically offset from one another in terms of absolute Sr/Ca values during overlapping intervals (Figure 2-2C; Table 2-2). The intercolony offsets in mean coral Sr/Ca range from -0.13 to +0.09 mmol/mol, relative to the centered composite of modern coral records (Figure 2-2B).

The distribution of observed intercolony offsets in coral Sr/Ca at Palmyra (±0.09mmol/mol; 1σ, n=5) is comparable to published intercolony offsets from *Porites* corals growing across the Line Islands [*Nurhati et al.*, 2009; *Carilli et al.*, 2014; *Alpert et al.*, 2016; *DeCarlo et al.*, 2016] and at other sites in the tropics [*Linsley et al.*, 2004; 2006; *Abram et al.*, 2008; 2009; *DeLong et al.*, 2011]. In total, the difference between the highest and lowest mean coral Sr/Ca value is 0.22mmol/mol, equivalent to ~4˚C when converted to SST using the published average coral Sr/Ca-SST calibration of 0.06mmol mol^{-1} $°C^{-1}$ [*Corrège*, 2006].

Table 2-2: Summary of statistics for coral Sr/Ca records.

	Sr/Ca (mmol/mol)				
Core	*Record Span*[a]	*Mean*	*Offset*[b]	*Seasonal Amplitude*	*Interannual Amplitude*
PM	1980-1998	8.96	-0.029	0.058 ± 0.016	0.043
PM1	1981-1998	9.06	-0.128	0.063 ± 0.019	0.042
PM5	1985-1998	8.87	0.064	0.058 ± 0.013	0.029
P13	1997-2007	8.84	0.089	0.061 ± 0.021	0.041
PAL2	2001-2010	8.93	0.004	0.054 ± 0.025	0.033

a) *interval across which Sr/Ca measurements were made*
b) *offset relative to the mean value of each coral across 1980-2010*

2.4.2 Sr/Ca-SST calibrations and uncertainties in Sr/Ca-based SST

Empirical Sr/Ca-SST calibration equations for Palmyra Atoll corals (Table 2-3) fall within the range of published calibrations for *Porites* corals [*Corrège*, 2006]. Calibration equations for each core (Figure 2-5) were computed using a weighted least-squares regression [*York et al.*, 2004], which accounts for uncertainty in both SST and coral Sr/Ca. The coral Sr/Ca-SST calibration slopes for cores PM, PM1, and PM5 (Figure 2-5A,B,C) are statistically identical at -0.118±0.003, -0.121±0.003, and -0.110±0.003 mmol mol^{-1} $°C^{-}$

[1], respectively. Cores P13 and PAL2 yield statistically different coral Sr/Ca-SST slopes (Figure 2-5D,E) of -0.072±0.002, and -0.061±0.002 mmol mol^{-1} °C^{-1}, respectively. The coral Sr/Ca composite yields a Sr/Ca-SST slope of -0.072±0.001 mmol mol^{-1} °C^{-1}, slightly steeper than the average coral Sr/Ca-SST slope of -0.06 mmol mol^{-1} °C^{-1} reported by *Corrège*, 2006. Intercepts for these coral Sr/Ca-SST calibrations range from 10.636±0.054 to 12.318±0.077, primarily reflecting the intercolony Sr/Ca offsets observed among these records.

Table 2-3: Relationships between coral proxies and SST.

	Sr/Ca vs SST			δ^{18}O vs SST	
Core	*slope[a] (mmol/mol ˚C^{-1})*	*intercept[a]*	*R*	*slope[a] (‰ ˚C^{-1})*	*R*
PM	-0.118 ± 0.003	12.318 ± 0.077	-0.72	-0.297	-0.79
PM1	-0.121 ± 0.003	12.516 ± 0.077	-0.76	-0.275	-0.84
PM5	-0.1 ± 0.003	11.726 ± 0.076	-0.70	-0.229	-0.83
P13	-0.072 ± 0.002	10.873 ± 0.047	-0.78	-	-
PAL2	-0.061 ± 0.002	10.637 ± 0.054	-0.81	-	-
Composite Sr/Ca	-0.073 ± 0.001	10.984 ± 0.033	-0.82	-	-

a) *slopes and intercepts computed using a weighted least squares regression [York et al.*, 2004*]*

Relative to the observed discrepancies in Sr/Ca-SST sensitivity among Palmyra corals, intercolony offsets are the largest source uncertainty in coral Sr/Ca-based temperature reconstructions. For a 0.1mmol/mol change in coral Sr/Ca (ΔSr/Ca), calibration slopes for PM, PM1, and PM5 predict similar change in SST of ~0.9˚C. For the same ΔSr/Ca of 0.1mmol/mol, the steeper calibration slopes for cores P13 and PAL2 predict larger temperature changes of 1.4˚C and 1.7˚C, respectively. Thus, applying a Sr/Ca-SST calibration derived from one core to coral Sr/Ca measurements from a different core could potentially over/underestimate SST variability by ±0.4˚C (1σ).

Applying the same Sr/Ca-SST calibration to cores from different colonies, as is often done for fossil coral-based records, can over/under estimate mean SST changes by ±1.2˚C (1σ). For a coral Sr/Ca value of 9.0mmol/mol, calibrations for cores PM, PM1, and PM5 yield temperatures of 28.1±0.1˚C, 29.0±0.1˚C, and 27.3±0.1˚C, respectively. For the same coral Sr/Ca value, calibrations for cores P13 and PAL2 yield temperature estimates of 25.7±0.2˚C and 27±0.2˚C, respectively. This spread in Sr/Ca-derived SST (±1.2˚C; 1σ) is an order of magnitude larger than the error of prediction for each calibration equation (±0.1 to ±0.2˚C, 1σ), highlighting analytical error alone is an inadequate measure of uncertainty in coral-derived temperature reconstructions.

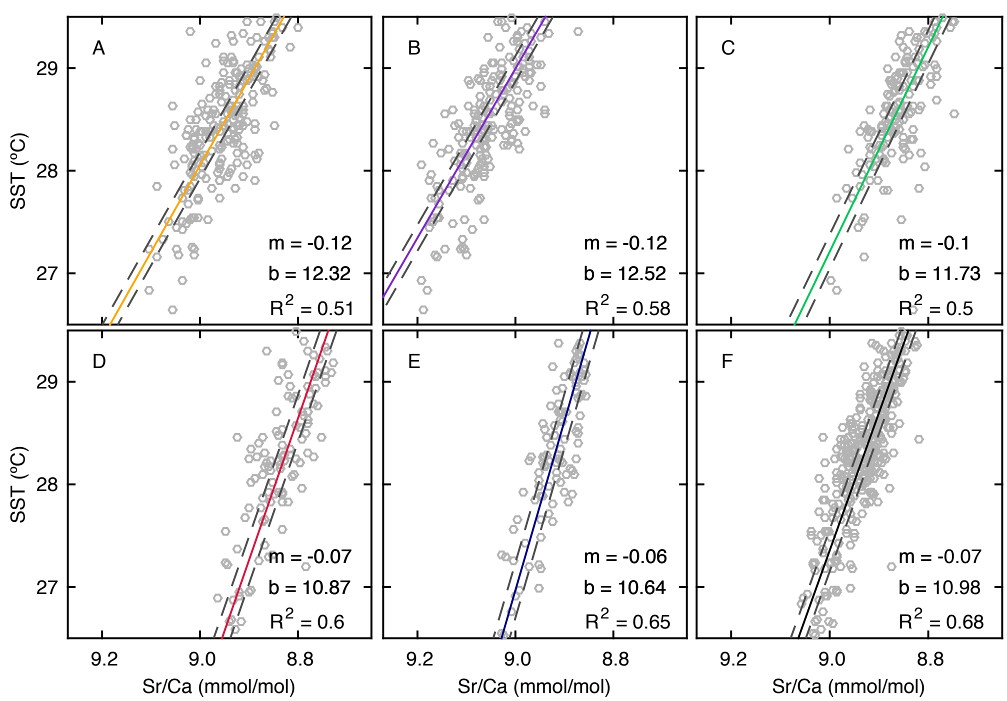

Figure 2-5: Coral Sr/Ca-SST calibrations for cores (A) PM, (B) PM1, (C) PM5, (D) P13, (E) PAL2, and (F) coral Sr/Ca composite. Coral Sr/Ca and SST pairs used in each calibration are shown in grey, *m* and *b* represent the slope and intercept for the equation Sr/Ca=*mSST + *b*, and dashed lines show 95% confidence intervals for each calibration.**

2.4.3 *Reproducibility among coral $\delta^{18}O$ records*

Monthly coral $\delta^{18}O$ records from Palmyra cores PM1, PM5 and PM (Figure 2-6A) are well-correlated to each other (R= 0.6 - 0.7, P<0.05) and with ERSST (R = -0.7 to -0.8, P<0.05, Table 2.-4). Between 1985-1998, the amplitude of seasonal cycles in coral $\delta^{18}O$ from cores PM and PM1 are statistically similar at 0.30±0.04‰ and 0.27±0.03‰, respectively (Figure 2-7A; Table 2-4). The amplitude of seasonal cycles in PM5 is lower 0.23±0.04‰ (Figure 2-7A), but still within error of cores PM and PM1. We estimate interannual $\delta^{18}O$ variability by removing the seasonal cycle, applying a 13-month running mean, and then calculating the standard deviation of each record. Interannual variability is consistent between cores PM1 and PM5 (±0.10‰, 1σ) between 1985-1998 (Figure 2-8). Across the same interval, core PM exhibits larger interannual variability (±0.13‰, 1σ), suggesting this colony might be more sensitive to ENSO. Obviously, longer coral $\delta^{18}O$ records would be required from each core in order to assess whether there is a systematic difference in the recording of interannual coral $\delta^{18}O$ variability for a given coral core, versus a slight underestimation of an isolated El Niño event. Unfortunately, such samples do not exist from Palmyra.

As with our coral Sr/Ca records, mean coral $\delta^{18}O$ values from cores PM, PM1, and PM5 are also systematically offset from each other (Table 2-4). These intercolony offsets (±0.016‰; 1σ) are an order of magnitude smaller than the ±0.12‰ (1σ) offsets observed among Palmyra fossil corals [*Cobb et al.*, 2003b] or offsets >0.2‰ observed at other sites [*Felis et al.*, 2003; *Grottoli and Eakin*, 2007; *Dassié et al.*, 2014]. Given that coral $\delta^{18}O$ is sensitive to SST, intercolony $\delta^{18}O$ offsets at Palmyra yield SST artifacts of ±0.1˚C (based on a $\delta^{18}O$-SST slope of 0.21‰ ˚C^{-1}) – an order of magnitude smaller than artifacts imparted by intercolony Sr/Ca offsets from the same cores.

While coral $\delta^{18}O$ is rarely used as an SST-only proxy, $\delta^{18}O$-SST slopes can be used as a metric to assess the sensitivity of coral $\delta^{18}O$ to climate across different colonies at the same site. As with coral Sr/Ca-SST calibrations, we use a weighted least-squares regression to compute $\delta^{18}O$-SST relationships for cores PM, PM1, and PM5 across the common interval of 1985 – 1998 (Table 2-3). Cores PM and PM1 yield statistically similar $\delta^{18}O$-SST slopes of -0.29±0.011 and -0.27±0.011‰˚C^{-1}, while core PM5 yields a lower slope of -0.23±0.011‰ ˚C^{-1}. For a change in coral $\delta^{18}O$ of 0.1‰ resulting from SST alone, slopes from cores PM and PM1 predict identical temperature changes of ~0.3˚C, while core PM5 predicts a nominally larger temperature shift of 0.4˚C.

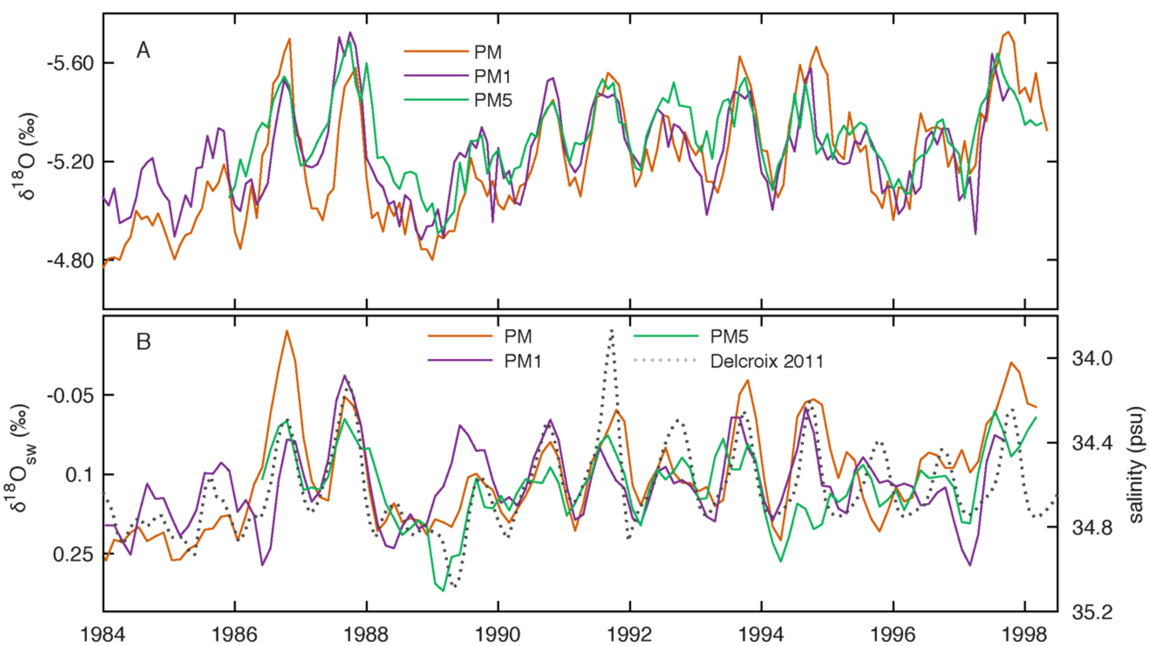

Figure 2-6: : Monthly $\delta^{18}O$ (A) and seasonal $\delta^{18}O_{sw}$ (B) from cores PM (orange), PM1 (purple), and PM5 (green). Seasonal derived are using paired Sr/Ca and coral $\delta^{18}O$

measurements from each core For comparison, seasonal sea-surface salinity for Palmyra from Delcroix et al., 2011 is plotted (black, dotted line).

Table 2-4: Summary of statistics for coral $\delta^{18}O$ records.

	$\delta^{18}O$ (‰)				
Core	*Mean*	*Record Span*[a]	*Offset*[b]	*Seasonal Amplitude*	*Interannual Amplitude*
PM	-5.240	1980-1998	-0.022	0.30 ± 0.04	0.13
PM1	-5.245	1983-1998	-0.017	0.27 ± 0.03	0.10
PM5	-5.301	1985-1998	0.039	0.23 ± 0.04	0.10

a) *interval across which Sr/Ca measurements were made*
b) *offset relative to the mean value of each coral across 1980-1998*

2.4.4 Reproducibility of coral-derived $\delta^{18}O_{sw}$ records

We derive three seasonally-resolved $\delta^{18}O_{sw}$ reconstructions using paired coral Sr/Ca and $\delta^{18}O$ measurements, from cores PM, PM1, and PM5, using procedures outlined in *Ren et al.*, 2003. As Sr/Ca and $\delta^{18}O$ analyses were performed on separate pulls of powder from each core (as opposed to splits of the same powder), we apply a 6-month running mean filter to minimize the influence of (i) small age model errors between the paired coral Sr/Ca and $\delta^{18}O$ records and (ii) analytical error. Following previous work at Palmyra Atoll [*Nurhati et al.*, 2009; 2011a], we calculate instantaneous changes in $\delta^{18}O_{sw}$ ($\Delta\delta^{18}O_{sw}$) using a $\delta^{18}O$-SST relationship of -0.21‰ C^{-1} [*Epstein et al.*, 1953] and the Sr/Ca-SST relationships for cores PM, PM1, and PM5 (-0.118, -0.121, and -0.100 mmol mol^{-1} $^{\circ}C^{-1}$, respectively) calculated above. Coral-derived $\Delta\delta^{18}O_{sw}$ values are highly correlated with each other (R=0.5), however $\Delta\delta^{18}O_{sw}$ amplitudes across individual seasons can vary among the three cores (Figure A-2). Coral-based $\delta^{18}O_{sw}$ records are then derived by integrating $\Delta\delta^{18}O_{sw}$ change over time.

Coral-based $\delta^{18}O_{sw}$ records are well correlated with each other (R=0.4 to 0.7, P<0.05; Figure 2-6B), and all three records generally agree with interpolated sea-surface salinity (R=0.5, P<0.5) from *Delcroix et al.*, 2011. The amplitude of seasonal cycles in the coral-based $\delta^{18}O_{sw}$ records are statistically similar across all three cores (0.11±0.02‰, 0.11±0.02‰, and 0.09±0.02‰; Figure 2-7B), however during certain years (e.g. 1995, 1987) the magnitude of reconstructed $\delta^{18}O_{sw}$ changes don't agree. The coral-based $\delta^{18}O_{sw}$ records are also slightly offset from each other (-0.027‰, 0.035‰, and -0.007‰ for PM, PM1, and PM5 respectively), a product of integrating slightly different $\Delta\delta^{18}O_{sw}$ values derived for each core.

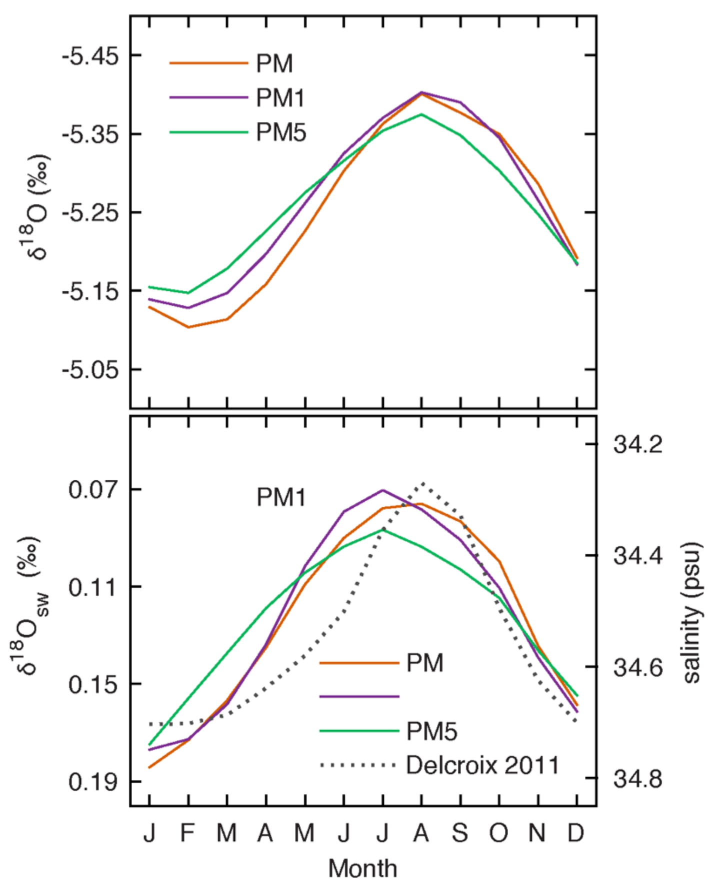

Figure 2-7: Amplitudes of seasonal cycles in (A) coral $\delta^{18}O$ and (B) coral-derived δ^{18}Osw records from cores PM (orange), PM1 (purple), and PM5 (green). Also plotted is the seasonal cycle in SSS at Palmyra (black, dotted line; Delcroix et al., 2011).

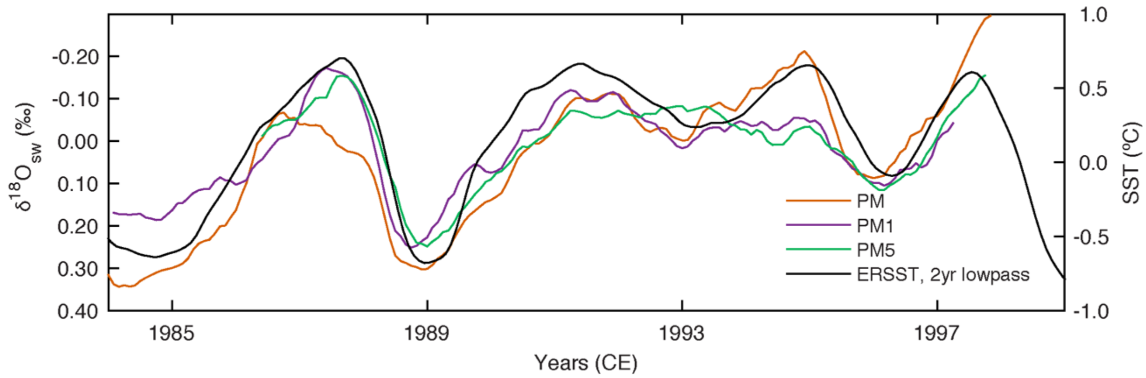

Figure 2-8: Interannual variability in coral δ^{18}O from cores PM (orange), PM1 (purple), and PM5 (green), estimated by removing seasonal cycles from monthly d18O and applying a 13-month running mean filter, compared with 2-yr low-pass filtered ERSSTv3b (black).

2.4.5 Potential sources of intercolony Sr/Ca and δ^{18}O variability

Intercolony Sr/Ca and δ^{18}O offsets observed at Palmyra cannot be explained by diagenesis, despite ample evidence that diagenesis can introduce significant artifacts in coral Sr/Ca and δ^{18}O records [*Sayani et al.*, 2011]. Diagenesis levels vary significantly on millimeter scales in any given coral core [e.g. *Bar-Matthews et al.*, 1993; *Hendy et al.*, 2007; *Hathorne et al.*, 2011], and typically produce large non-climatic fluctuations in coral Sr/Ca and δ^{18}O instead of the uniform offsets observed in our ensemble of modern coral records. Furthermore, with the exception of the pre-1997 section of P13, SEM images do not show any evidence of significant or consistent alteration in any of the remaining cores (Figure A-3).

SST variability across an individual reef has been linked to intercolony Sr/Ca variability at some sites [e.g. *Alpert et al.*, 2016]. The lack of *in situ* SST data from the exact coral core locations at Palmyra prevents us from directly comparing SST variability with intercolony variability across our cores. However, temperature loggers deployed around Palmyra Atoll (Figure 2-1) by NOAA CREP from 2007-2011 suggest that spatial temperature variability across the western reef terrace, where four of our cores were drilled, is ±0.1°C (1σ). This spatial SST variability is an order of magnitude smaller than the ±1˚C temperature variability needed to produce the ±0.9mmol/mol (1σ) offsets observed between PM, PM1, and PM5.

Skeletal extension and/or calcification rates are often invoked to explain, and in some cases correct for [*Maier et al.*, 2004; *Goodkin et al.*, 2005; 2007], intercolony Sr/Ca and $\delta^{18}O$ offsets in a variety of coral species [e.g.*de Villiers et al.*, 1995a; *Alibert and McCulloch*, 1997; *Lough and Barnes*, 1997; *Cohen and Hart*, 2004; *Suzuki et al.*, 2005; *Goodkin et al.*, 2007; *Kuffner et al.*, 2012]. Coral biomineralization models suggest that corals incorporate less Sr^{2+} relative to Ca^{2+} when they calcify faster, and vice versa [*Gaetani and Cohen*, 2006], consistent with experiments that manipulate inorganic aragonite precipitation rates [*Holcomb et al.*, 2009]. As such, faster growing colonies would have lower Sr/Ca values, while corals that are growing much slower would have higher Sr/Ca values. Studies examining large numbers of colonies, primarily from the Great Barrier Reef, do indeed show a relationship between extension rate and mean SST, extension rate and mean Sr/Ca, and calcification rate and mean Sr/Ca [e.g. *Lough and Barnes*, 1997; *Lough and Cooper*, 2011]. However, our data do not show any statistically significant relationships between coral Sr/Ca and extension rates (R=0.29, P=0.63, n=5), or between coral $\delta^{18}O$ and extension rates (R=0.9, P=0.2, n=3) on the modern-day reef at Palmyra Atoll.

2.5 Discussion and Conclusion

Our results demonstrate that overlapping coral Sr/Ca and $\delta^{18}O$ records from Palmyra Atoll reproduce similar climate variability on monthly-interannual timescales, but these records exhibit different proxy-SST sensitivities and their mean values are statistically offset. Of these two types of intercolony variabilities, our results confirm that intercolony offsets represent a significantly larger uncertainty compared to proxy-SST slopes (±1.2˚C vs ± 0.4˚C). Without a clear explanation for intercolony variability among Palmyra corals, and no objective means of correcting for this variability, we are left to speculate that vital effects produce systematically different Sr/Ca and $\delta^{18}O$ signals in corals growing on the same reef. We reiterate that intercolony variability has virtually no impact on estimates of climate change inferred from differences in coral geochemistry within a core, which represent the vast majority of coral $\delta^{18}O$, coral Sr/Ca, and coral-based $\delta^{18}O_{sw}$ records. However, when comparing coral records from different colonies, as is routinely done when reconstructing climate beyond the timeframe afforded by a living *Porites* colony, intercolony offsets in Sr/Ca and $\delta^{18}O$ prevent us from resolving SST changes smaller than ±1.2˚C and ±0.1˚C, respectively. This is particularly problematic at sites such as Palmyra, where decadal-to-centennial scale temperature variability across much of the Holocene is expected to be <2˚C, and given that estimates for glacial-interglacial changes in SST across the tropical Pacific do not exceed 4˚C [*Visser et al.*, 2003; *Koutavas and Joanides*, 2012].

Recent studies have demonstrated that local to regional composites, which employ proxy records from multiple overlapping modern or fossil corals, can be used to isolate common climate signals, vastly improving the robustness of coral-based climate reconstructions [e.g. *Hendy*, 2002; *Lough*, 2004; *Stephans et al.*, 2004; *Cahyarini et al.*, 2008; *DeLong et al.*, 2013; *Dassié et al.*, 2014]. Building on this composite approach, we outline a strategy for reducing uncertainties stemming from intercolony offsets across multiple coral colonies. The existence of similar intercolony offsets in *Porites* corals from multiple sites suggests that for any given temperature, there exists a finite range of possible coral Sr/Ca and $\delta^{18}O$ values distributed about a mean. At Palmyra, the spread in mean coral Sr/Ca values is ±0.085mmol/mol (1σ) and the spread in mean coral $\delta^{18}O$ is ±0.1‰ (1σ) for overlapping sections of core. If we assume the spread in intercolony offsets is defined by a normal distribution (and there are no data to support non-normal distributions), one can use multiple, overlapping corals to constrain the average temperature for a given time period to a desired level of accuracy. Specifically, the uncertainty of any multi-coral composite compiled across a given time period scales by $\sqrt{N}$, where N is the number of overlapping corals used to construct a climate record. Thus with 5 coral cores, the uncertainty associated with any estimate of mean climate from that ensemble of cores is reduced by a factor of $\sqrt{5}$, from ±0.085 mmol/mol (1σ) to ±0.038 mmol/mol (1σ). In terms of SST, the uncertainty for this hypothetical coral composite is reduced from ±1.2 to ±0.5˚C (1σ). Therefore, to resolve a SST change of <1˚C, such as that which may have occurred during the Little Ice Age (LIA; 1500-1850) in the central tropical Pacific [*Emile-Geay et al.*, 2013], we would need at least 5 corals that date to within the LIA to compare with the 5 corals we have from the late 20th century.

In summary, intercolony variability is a significant source of uncertainty in coral-based reconstructions, however replicating coral proxy records, using multiple colonies that span any time periods of interest, can substantially improve the utility of these reconstructions. This approach significantly increases the number fossil corals and accompanying geochemical analyses needed to complete a single reconstruction of mean climate during the pre-industrial era, and may not be a practical strategy for all sites. For sites like Palmyra Atoll and neighboring Kiritimati Island (Christmas Island, (2˚N, 157˚W), where large numbers of fossil corals with similar ages exist [*Cobb et al.*, 2003a; *Grothe et al.*, 2016], the composite approach outlined here would provide robust, quantitative, well-replicated paleoclimate records and associated uncertainties. New coral SST proxies currently under development, such as Sr-U [*DeCarlo et al.*, 2016] and Li/Mg [*Hathorne et al.*, 2013b], hold great promise but may also be subject to intercolony offsets such as those documented for coral Sr/Ca and coral $\delta^{18}O$ [e.g. *Fowell et al.*, 2016]. Clearly extensive, multi-colony replication studies such as that presented here are also needed for these new coral proxies. Such replication studies deliver quantitative constraints on the magnitude of intercolony offsets and differences in proxy-SST calibration slopes, even though they rarely reveal the underlying causes of the differences between neighboring colonies.

2.6 Acknowledgements

We thank the NOAA Coral Reef Ecosystem Program for collecting one of the cores and *in situ* temperature data from Palmyra Atoll. We also thank Anne Cohen and Thomas DeCarlo for providing coral material used here, Yolande Berta and Georgia Tech's Center for Nanostructure Characterization for providing access to their SEM facility, and Christopher R. Maupin for assistance with mass spec repairs. ERSST V3b data provided by the NOAA PSD, Boulder, Colorado, USA, from their Web site at http://www.cdc.noaa.gov/.

CHAPTER 3. RELIABLE CORAL SR/CA ESTIMATES FROM AN ALTERED FOSSIL CORAL USING SIMS

3.1 Abstract

Fossil corals are one of the few marine archives that provide monthly-to-annually resolved paleoclimate records. However, the accuracy of these reconstructions can be severely compromised by diagenesis. Secondary ion mass spectrometry (SIMS) offers the ability to sample at very high-resolutions, and has been used with some success to target analyze only pristine material within altered fossil corals. Here we demonstrate the utility of this technique for extracting more reliable Sr/Ca-based temperature estimates from altered fossil corals. In overlapping samples from three modern corals, we are able to reproduce bulk Sr/Ca estimates within 0.3% using only 3-4 SIMS analyses per month of coral growth. Across three different sampling transects in these modern corals, smoothed SIMS data largely reproduce monthly SST variability. Application of this technique to lightly-altered sections of a young fossil coral suggests that the diagenesis we observe here does not impact fidelity of bulk Sr/Ca estimates. However, in heavily-altered section of the same coral, where bulk Sr/Ca estimates yield temperatures that are ~6˚C too cool, targeted analyses of only pristine material provides both mean Sr/Ca estimates and a ~4yr time series that are consistent with SST. Given that all fossil corals exhibit some level of diagenesis, and that even 1% of infilling can produce artifacts of 1-2˚C, microscale analyses may be a powerful tool for verifying the accuracy of conventional Sr/Ca measurements.

3.2 Introduction

Massive corals are one of the few marine archives that offer monthly-to-annually resolved records of past tropical climate and environmental variability spanning recent centuries [e.g. *Hendy*, 2002; *Nurhati et al.*, 2011a; *DeLong et al.*, 2012; *Linsley et al.*, 2015; *Thompson et al.*, 2015]. Fossil corals allow us to further extend these reconstructions of tropical climate variability across the Holocene [e.g. *Beck et al.*, 1997; *Cobb et al.*, 2003b; *DeLong et al.*, 2010; *Cobb et al.*, 2013; *McGregor et al.*, 2013; *Toth et al.*, 2015], and can even provide unique snapshots of seasonality and interannual variability across the last glacial cycle [e.g. *Tudhope*, 2001; *Corrège et al.*, 2004; *Felis et al.*, 2014b], the previous interglacial [*Hughen et al.*, 1999], and as far back as the Miocene [*Weiss et al.*, 2017].

Most coral-based climate reconstructions rely on the oxygen isotopic composition ($\delta^{18}O$) of coral skeletons – which varies as a function of SST and the $\delta^{18}O$ of seawater. Coral Sr/Ca ratios serve as a proxy for SST that can be applied in isolation [*Weber*, 1973; *Beck et al.*, 1992], or in combination with coral $\delta^{18}O$ [e.g. *Ren et al.*, 2003] to reconstruct changes in seawater $\delta^{18}O$ (itself proxy for salinity). As such, the number of coral Sr/Ca records has increased dramatically in recent years, with the promise of delivering quantitative reconstructions of climate variables of interest to climate dynamicists and modelers. To date, the vast majority of coral Sr/Ca records are recovered from so-called modern corals, drilled from living coral colonies, while only a handful of coral Sr/Ca records exist from fossil corals [e.g. *Corrège et al.*, 2004; *Felis et al.*, 2014a; *Toth et al.*, 2015].

Fossil corals contain varying levels of diagenetic alteration, most often in the form of surface coatings of aragonite and/or calcite cements, which leads to large biases in fossil coral–based reconstructions of climate [e.g. *Bar-Matthews et al.*, 1993; *Enmar et al.*, 2000; *Müller et al.*, 2001; *Ribaud-Laurenti et al.*, 2001; *McGregor and Gagan*, 2003; *Quinn and Taylor*, 2006; *Allison et al.*, 2007; *Hendy et al.*, 2007]. Even with thorough screening, small quantities of diagenetic material can be inadvertently included in drilled samples, as the areas of a core screened for alteration are often some distance away from the sampling transect used for geochemical analyses. The inclusion of even 2% of secondary aragonite cements, which have a much higher $\delta^{18}O$ and Sr/Ca composition than coral aragonite, can introduce artifacts of ~0.6˚C in coral $\delta^{18}O$-based reconstructions and ~1˚C in coral Sr/Ca-based reconstructions [*Allison et al.*, 2007; *Sayani et al.*, 2011]. Secondary calcite cements, another common alteration phase found in fossil corals, have a more variable Sr/Ca composition that largely depends on how these cements were formed [*Rabier et al.*, 2008]. However, the inclusion of even 2% of secondary calcite cements can produce warm artifacts of up to ~2˚C in coral Sr/Ca records [*Sayani et al.*, 2011]. While alteration is more common in older fossil corals, diagenesis has been observed in live corals within 5yrs following deposition of the original skeleton [*Nothdurft and Webb*, 2008]. Diagenesis is very heterogeneous in both modern and fossil corals [e.g. *Bar-Matthews et al.*, 1993; *Hendy et al.*, 2007; *Hathorne et al.*, 2011], varying significantly on mm-scales, which means that (i) it can go undetected in screening procedures, and (ii) whole-coral corrections for diagenesis are not possible.

Microscale analytical techniques, such as secondary ion mass spectrometry (SIMS), allow us to capitalize on this patchy nature of diagenesis and extract reliable Sr/Ca estimates from altered coral by selectively sampling only pristine coral material. This potential rests on the fact that most diagenetic phases present as surface coatings that leave the interior of the coral skeleton geochemically intact, provided that dissolution is minimal. Early application of SIMS to altered fossil corals from the tropical western Pacific demonstrate that SIMS Sr/Ca analyses yield temperature estimates for the last deglacial that are consistent with other SST reconstructions from the region [*Cohen and Hart*, 2004; *Allison*, 2005]. While these studies highlight that SIMS can be used to check the accuracy of drilled Sr/Ca records, there have been no substantial attempts generating reliable Sr/Ca-based SST time series from altered fossil corals using this technique. Even within modern corals, only *Allison and Finch*, 2009 has explored the ability to extract reliable and reproducible Sr/Ca-based SST records using discrete SIMS analyses.

Beyond the time- and cost-intensive nature of SIMS analyses, the largest barrier to the application SIMS Sr/Ca high μm-scale variability in the geochemical composition of coral aragonite [*Allison*, 1996a; *Hart and Cohen*, 1996; *Sinclair et al.*, 1998; *Meibom*, 2003; *Rollion-Bard et al.*, 2003a; *Gagnon et al.*, 2007; *Allison and Finch*, 2010]. Geochemical composition varies considerably between different features of the coral skeleton [*Cohen et al.*, 2001; *Allison and Finch*, 2004; *Gagnon et al.*, 2007]. However, even along the same skeletal feature, large fluctuations are observed in Sr/Ca composition that far exceed variability observed in parallel drilled Sr/Ca measurements and cannot be explained by local temperature or environmental variability on daily-weekly times scales [e.g. *Meibom*, 2003; *Meibom et al.*, 2008]. Furthermore, these μm-scale fluctuations are neither reproducible between parallel SIMS sampling tracks on the same coral, nor between sampling tracks in overlapping corals [*Allison and Finch*, 2009]. While microscale coral geochemistry can't be used to construct daily to weekly resolved climate records, averaging multiple SIMS analyses reproduces drilled Sr/Ca values across the same time period [*Cohen and Hart*, 2004; *Allison*, 2005; *Sayani et al.*, 2011]. More promising, however, is that smoothing microscale Sr/Ca measurements may isolate monthly variability typically observed in drilled Sr/Ca records and local SST [e.g. *Allison and Finch*, 2004; *Sinclair*, 2005]. As such, targeted analyses of pristine skeletal material should yield reliable Sr/Ca-based estimates of SST.

In this study, we explore the reproducibility of SIMS Sr/Ca analyses across three overlapping modern coral samples, with an emphasis on generating high-fidelity records using as few SIMS analyses as possible. Using the sampling methodology developed for these modern corals, we attempt to extract reliable Sr/Ca-based temperature estimates young fossil coral with varying degrees of alteration. This particular fossil coral, NB9, which grew from 1908 to 1938, is the ideal test candidate as temperature data (from ERSSTv3b) is available to assess the quality of the SIMS results. Finally, we comment on utility of microscale analytical techniques for improving the fidelity of coral-based paleoclimate reconstructions.

3.3 Methods

We present SIMS Sr/Ca measurements across 3yr-long transects from three overlapping Porites corals, collected live from Palmyra Atoll (5°53'N, 162°5'W) in May 1998. We also present a ~30yr-long drilled Sr/Ca record, and SIMS Sr/Ca analyses across three different transects, from a fossil Porites coral also collected from Palmyra. The modern corals, PM, PM1, and PM5, serve as ideal candidates for testing and refining our

SIMS methodology as they have been previously vetted for diagenesis and used to develop monthly coral Sr/Ca and oxygen isotope records [*Cobb et al.*, 2001; *Nurhati et al.*, 2009; 2011a; Sayani et al., in prep]. U/Th dates and oxygen isotope data from the well-preserved section of fossil coral NB9 are presented in *Cobb et al.*, 2003a and *Cobb et al.*, 2003b, respectively.

3.3.1 Conventional Sr/Ca analyses and diagenesis screening

Coral cores were slabbed and prepared for geochemical analyses using standard procedures. For "bulk" or drilled Sr/Ca analyses, coral powders were milled at 1mm intervals from each coral slab, along a transect parallel to the primary growth axis, and then digested in 2-2.7mL of 2% trace-metal grade HNO_3 to obtain create solutions with ~30ppm calcium. The Sr/Ca of each solution was measured using a Horiba Jobin-Yvon Ultima 2C Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) located at Georgia Tech. Samples were bracketed with an internal standard, used to correct for instrumental drift within a run, and obtain analytical precisions < ±0.1% or ±0.09mmol/mol (1σ) [*Schrag*, 1999]. Repeated analysis, 3-5 per run, of a coral-derived standard is used ensure minimal long-term drift across different analyses sessions. Coral Sr/Ca values reported here are not corrected to JCp-1 [*Hathorne et al.*, 2013a], however periodic analyses of this standard using our analytical setup is 8.99+0.01mmol/mol (n=25). Coral Sr/Ca ratios for fossil coral NB9 are converted to SST using the Sr/Ca-SST calibration derived for core PM by *Sayani et al., in prep*:

$$Sr/Ca = (-0.118 \pm 0.0027)*SST + 12.318 \quad (1)$$

Potentially altered horizons of core NB9 were identified through visual examination of the coral slab, density anomalies within x-rays, and any departures of drilled Sr/Ca values from SST. To check of the presence of diagenesis in these potentially altered sections of NB9, and the preservation of potentially non-altered sections of NB9, we extracted small (2-4mm) coral chunks near the drilled Sr/Ca transect on each slab. These coral chunks were prepared for imaging with a scanning electron microscope (SEM) following procedures outlined in *Sayani et al.*, 2011. SEM images were obtained using either a Hitachi S-800 field emission gun SEM or a LEO 1530 thermally-assisted field emission SEM located at Georgia Tech.

3.3.2 SIM sample preparation

We prepared 2-3 continuous thin sections across intervals of interest from each core. Thin sections were prepared by cutting a 4-6cm long coral segment from each slab, typically within 1-3 cm from the transect used for drilled Sr/Ca analyses. Each coral segment was lightly scored on the back and snapped by hand, into ~1cm pieces, to preserve continuity across the sampling surface. Coral segments were then embedded in epoxy, sectioned at similar depths, polished and mounted onto 1-inch rounds, and then polished again to a final thickness of at least ~30 µm. Prior to SIMS analyses, each thin section was gold coated using standard procedures, and then imaged using a transmitted and reflected light microscope to identify and map potential sampling transects that are continuous through sequential thin sections.

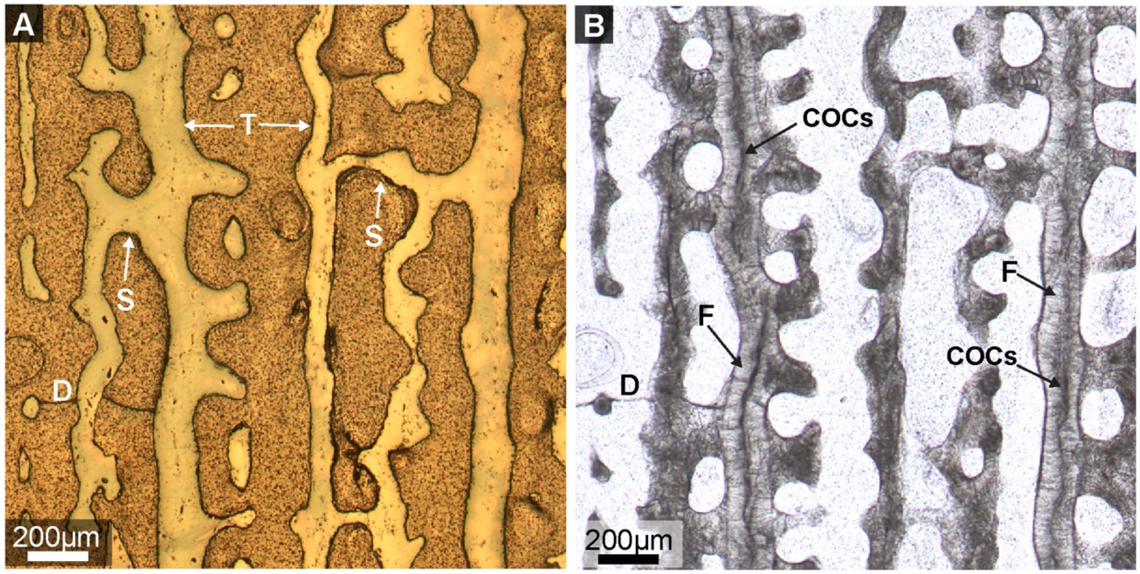

Figure 3-1: Examples of µm-scale skeletal features within a corallite. The gold-coated image (A) shows the trabeculae (T) and synapticulae (S) which form mm-scale features of the corallite. In the transmitted light image (B), we see that the trabeculae, themselves are composed of micron-sized centers of calcification (COCS), from which tightly bundled aragonite fibers (F) radiate outwards.

3.3.3 Coral Skeletal Structure and SIMS Sr/Ca analyses

Individual coral polyps are housed within a corallite, a mm-scale skeletal feature composed of the thecal wall, which forms a perimeter around the polyp, and the septa, which extend inwards to the center of the corallite (see figure 2 in *Rabier et al.*, 2008). At sub-mm scales, the septa and theca resemble scaffolds with vertical sections called trabeculae, and horizontal sections called synapticulae (Figure 3-1A). With ion beam diameters as small as 10µm, SIMS analyses measure spots within these trabeculae and synapticulae. At µm-scales, all coral skeletal features are formed by micron-sized crystals, commonly referred to as the "centers of calcification" (COCs), from which dense bundles of aragonite fibers radiate outwards [*Cohen et al.*, 2001 and references therein]. COCs and aragonite fibers have distinct geochemical compositions, with COCs being more enriched in Sr [e.g. *Cohen et al.*, 2001; *Meibom et al.*, 2008]. As fibers account for up to >95% of the coral skeleton, we try to avoid sampling any COCs during our analyses.

SIMS Sr/Ca measurements were made using a Cameca IMS-1280 ion microprobe, located at the Northeast National Ion Microprobe Facility (NENIMF) at the Woods Hole Oceanographic Institute, equipped with a ~6nA O^- ion beam, accelerated at 10keV. SIMS can be used to analyze spots as small as 10μm in diameter, however, we employ ~20μm diameter beam to average more coral material in each analyses. Using this beam size, we measured Sr/Ca ratios along pristine trabeculae, targeting spots between the COCs and the edge of the trabeculae. Secondary charged ions with masses corresponding to ^{42}Ca and ^{88}Sr were measured using a -80eV energy filter. Following a pre-analyses burn time of 90s to remove gold coating, we measured ^{42}Ca across 10 cycles lasting 10s each, and collected measured ^{88}Sr across 10 cycles lasting 15s each. As all masses were measured on a single collector, we used a dead-time interpolation scheme to correct for any drift or reduction in counts across the analyses period. Analytical uncertainty for individual analyses are derived from estimated as the standard error of ^{88}Sr/^{42}Ca measurements across the 9 remaining cycles, range from 0.01 to 0.05mmol/mol (1σ).

To convert measured intensities for ^{42}Ca and ^{88}Sr to [Ca] and [Sr], we built a calibration curve at the beginning of each day using 3-5 measurements on three different standards - an OKA Carbonatite crystal, a calcite crystal (Blue-0875) and an aragonite crystal (AG1) – whose Sr/Ca ratios (0.56-19.3mmol/mol) have been previously quantified via ICP-MS [*Gaetani and Cohen*, 2006]. SIMS data was collected over four sessions, from 2012 to 2016, with an average reproducibility of ±1.4% for OKA, ±2.4% for AG1, and

±2.3% for Blue-0875 per session. Reproducibility of standards reported reflect compositional heterogeneity within each crystal in addition analytical precision. To generate smoothed SIMS Sr/Ca time series, we removed data points that were ±2σ outside mean of all analyses from each core, then applied an 11-point running mean filter to the remaining data. Uncertainty in smoothed SIMS Sr/Ca is estimated by calculating the standard error of all points used to calculate the running mean at each time step. As depth-age relationships already exists for all the cores we used, we were easily able to map the location of each SIMS measurement onto core depth, and subsequently derive an age model for each SIMS record. Using the smoothed SIMS Sr/Ca time series calculated for each core, we manually fine-tuned SIMS chronology for cores PM1 and PM, by shifting a subset of points by 0.1-1mm to improve visual correspondence with either an overlapping drilled Sr/Ca record or ERSSTv3b. In general, we avoided fine-tuning SIMS chronologies as these records are derived by smoothing 2-4 analyses per month.

3.4 Results

3.4.1 Sampling strategy for deriving SIMS Sr/Ca records

COCs are not always located in the center of a trabecula, especially in more complex skeletal structures near the thecal wall. We also cannot distinguish between COCs and aragonite fibers on gold-coated thin sections that loaded on the SIMS (Figure 3-1). To assess the impact of any accidental inclusion of micron-sized COCs in our SIMS analyses, we measure spots containing COCS, and the fibers adjacent to these spots, at 7 locations on a 2mm-long transect in core PM. Analyses on the fibers only yield a mean Sr/Ca value of 8.95±0.02mmol/mol (1σ, n=14), consistent with the average drilled Sr/Ca values measured across this horizon (8.95±0.04mmol/mol, 1σ, n=3). In contrast, analyses that include COCs produce an ~2% higher mean Sr/Ca value of 9.15±0.03mmol/mol (1σ; n=7). To minimize the impact of COCs on any of the metrics or smoothed SIMS data presented here, we remove any SIMS Sr/Ca measurements that are ±2 standard deviations outside the mean.

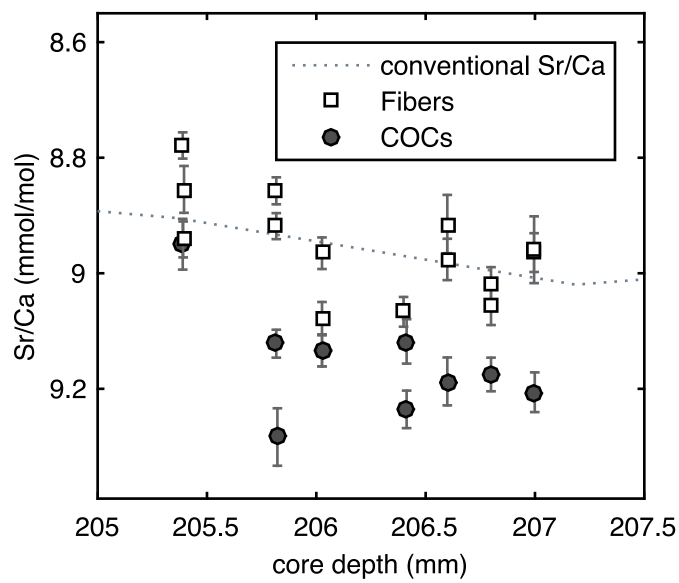

Figure 3-2: SIMS Sr/Ca analyses on COCs (filled circles) and adjacent fibers (open squares) compared to conventional ICP-OES Sr/Ca measurements from core PM (dashed line). Error bars (1s) represent analytical error for individual SIMS measurements.

To generate a SIMS Sr/Ca time series spanning 1987-1988 from core PM, we measured Sr/Ca along an ~18mm transect at ~200μm intervals, targeting simple trabeculae where the location of COCs were more apparent (Figure 3-2). Each ~20μm spot measurement averages ~half a day's worth of skeletal growth, and each measurement is spaced 3-4 days apart. Consistent with previous studies [e.g. *Allison and Finch*, 2009], SIMS measurements along this transect are characterized by large point-to-point Sr/Ca variations of ~0.6mmol/mol, which far exceed diurnal SST variability (1.5˚C or

0.1mmol/mol) at our site. However, the average of these SIMS Sr/Ca measurements (8.99±0.02mmol/mol, n=80) is equivalent to drilled Sr/Ca measurements across the same interval (8.97±0.02mmol/mol, n=20). We find that an 11-point running mean filter, equivalent to ~3 months, yields a time series with variability similar to that of monthly drilled Sr/Ca. We observe no discernable benefit to sampling at ~200um intervals, as measurements taken every ~400um and smoothed with an 11-point running mean filter also reproduce monthly drilled Sr/Ca.

Sampling every ~400um, we extend the SIMS Sr/Ca transect from core PM across two more years (Figure 3-3A). The average Sr/Ca value of individual SIMS analyses across the entire 1985-1988 interval, 8.99±0.01mmol/mol (n=123), is equivalent to the average drilled Sr/Ca value of 8.98±0.01mmol/mol (n=56). The smoothed SIMS Sr/Ca time series from core PM (Figure 3-3A) closely tracks both drilled Sr/Ca from this core and ERSSTv3b across the same time period.

3.4.2 Reproducibility of SIMS Sr/Ca analyses across overlapping modern corals

We measured Sr/Ca at ~400um intervals between 1986-1989 in core PM5 (Figure 3-3B), and between 1986-1989 and 1995-1997 in core PM1 (Figure 3-3C, 3-3D). Across their respective intervals, individual SIMS Sr/Ca measurements from both core PM1 and PM5 are also characterized by fine-scale fluctuations ranging from ~0.6mmol/mol to ~0.7mmol/mol. Between 1985-1989, there are no significant correlations between the overlapping SIMS transects. The average of individual SIMS Sr/Ca measurements between 1986-1989 in core PM1, 9.02±0.01mmol/mol (n=114), is within range of the average of drilled Sr/Ca, 9.04±0.01mmol/mol (n=45), across the same time period. Likewise, between

1995-1997, the average SIMS Sr/Ca in core PM1, 9.05±0.02mmol/mol (n=85), is consistent with drilled Sr/Ca, 9.06±0.01mmol/mol (n=38), across the same interval. SIMS analyses from the 1986-1989 horizon of PM5 yield an average Sr/Ca value (8.89±0.01mmol/mol; n=84), that is slightly higher but still within error of drilled Sr/Ca from this core (8.86±0.01mmol/mol; n=46). The mean values of drilled Sr/Ca records from cores PM, PM1, and PM5 are systematically offset by ±0.08mmol/mol (1σ), with core PM1 exhibiting absolute the highest Sr/Ca values and core PM5 exhibiting the lowest absolute Sr/Ca values [Sayani et al., in prep]. Our SIMS measurements produce similar intercolony offsets of ±0.07mmol/mol (1σ), with core PM1 exhibiting higher Sr/Ca values and core PM5 exhibiting the lowest Sr/Ca values.

Smoothed Sr/Ca SIMS measurements from core PM1 reproduce variability observed in both the drilled Sr/Ca record from this core (Figure 3-3C, 3-3D). This is not the case for core PM5, where between 1987-1988, the smoothed Sr/Ca diverges from both this core's drilled Sr/Ca record and SST (Figure 3-3B). Careful examination of the SIMS transect from PM5 between 1986-1987 reveals that multiple analyses included COCs, yielding much higher Sr/Ca values. Nonetheless, smoothed SIMS Sr/Ca from PM, and both transects in PM1, reproduce SST variability (R=-0.5 to -0.8).

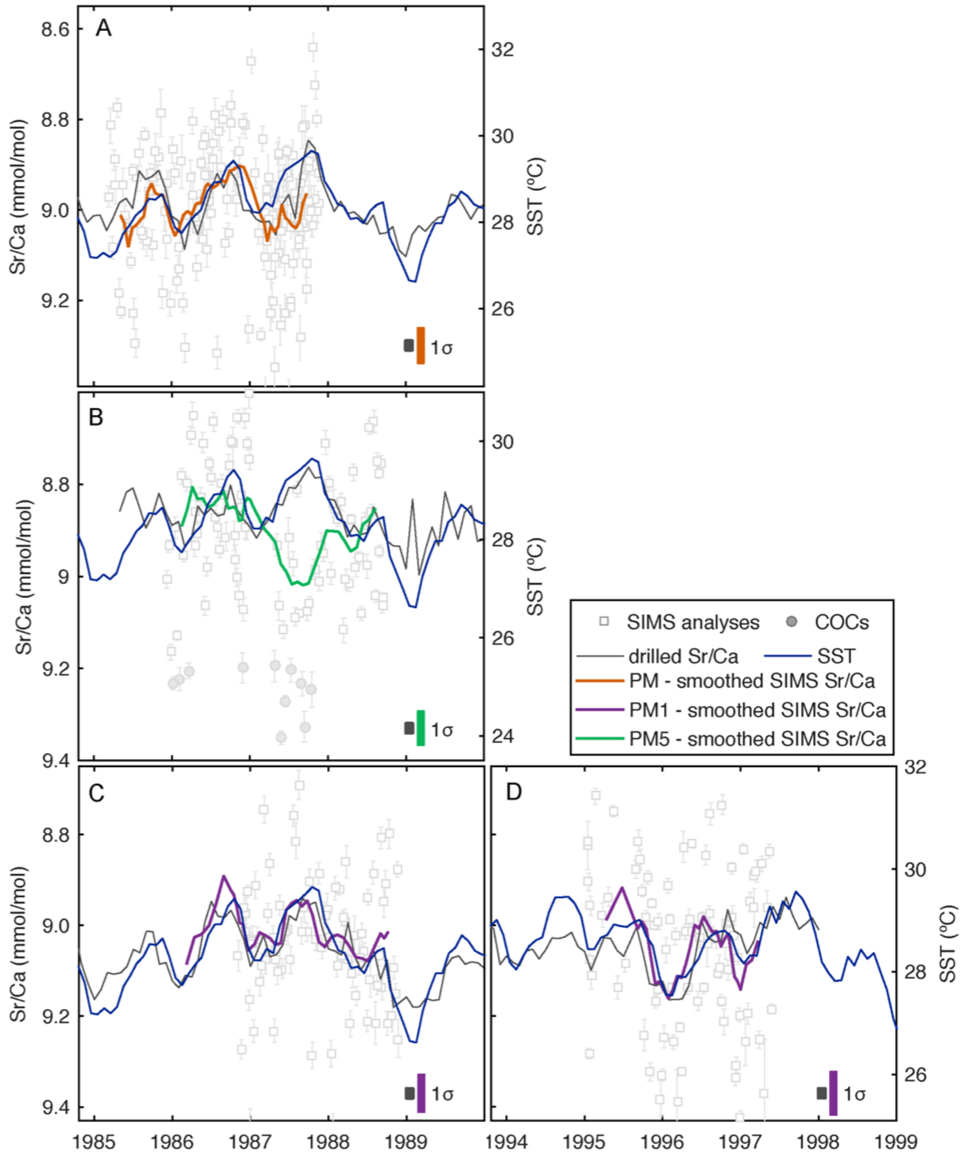

Figure 3-3: Smoothed SIMS Sr/Ca from cores PM (A; orange line), PM1 (B; purple line), and PM5 (C; green line), compared ERSSTv3b (blue line) and drilled Sr/Ca from each core (grey line). Also plotted are individual SIMS analyses (squares) used to derive the smoothed SIMS Sr/Ca time series for each core. Filled circles denote individual SIMS analyses that are removed prior to smoothing.

3.4.3 *Selective SIMS analyses of an altered fossil coral*

Drilled Sr/Ca from core NB9 largely tracks ERSST between 1917-1935 (R=-0.6; Figure 3-4) and an overlapping drilled Sr/Ca record from core PM (R=0.5). While there are no large excursions from SST across this horizon of NB9, we observe intervals where drilled Sr/Ca reconstructs temperatures that are on average 1˚C cooler than ERSST (e.g. around 1918, 1922, 1928, and 1930). SEM images from this horizon of NB9 reveal generally well preserved surfaces with patches of small (<5μm-long) secondary aragonite needles and very minor dissolution (Figure 3-6A, 3-6B). Between 1911-1917, drilled Sr/Ca from core NB9 diverge from ERSST, reaching a maximum excursion of -0.63mmol/mol in 1914. Across this ~6 year period, drilled Sr/Ca from core NB9 implies temperatures were 1-6˚C cooler. SEM images from this horizon of the core reveal more consistent coverage of ~10um-long secondary aragonite needles (Figure 3-6C). The inclusion of these needles in coral powders used for ICP-OES measurements likely produce the anomalously high Sr/Ca values we observe in the bulk measurements.

We generate SIMS time series from three different horizons of NB9: (i) 1931-1933, where drilled Sr/Ca matches SST, (ii) 1920-1922, where drilled Sr/Ca contains a cool excursion of ~1˚C (Figure 3-4), and (ii) 1911-1914, where the core has consistent alteration (Figure 3-6C) and drilled Sr/Ca has large excursions from SST. Across 1931-1935, SIMS analyses yield an average Sr/Ca value of 9.10±0.02mmol/mol (n=78), equivalent to the average of drilled Sr/Ca (9.08±0.01mmol/mol; n=33). Both conventional and SIMS Sr/Ca yield temperature estimates, 27.4±0.05˚C and 27.2±0.2˚C respectively, that are consistent with the average of ERSST (27.4˚C) across this interval. Between 1920-1922, the average SIMS Sr/Ca analyses, 9.09±0.02mmol/mol (n=73), is also consistent with drilled Sr/Ca

(9.07±0.01mmol/mol; n=31). Both drilled and SIMS Sr/Ca yield temperatures, 27.3±0.2˚C and 27.5±0.1˚C respectively, that are slightly cooler than corresponding ERSST (27.7˚C).

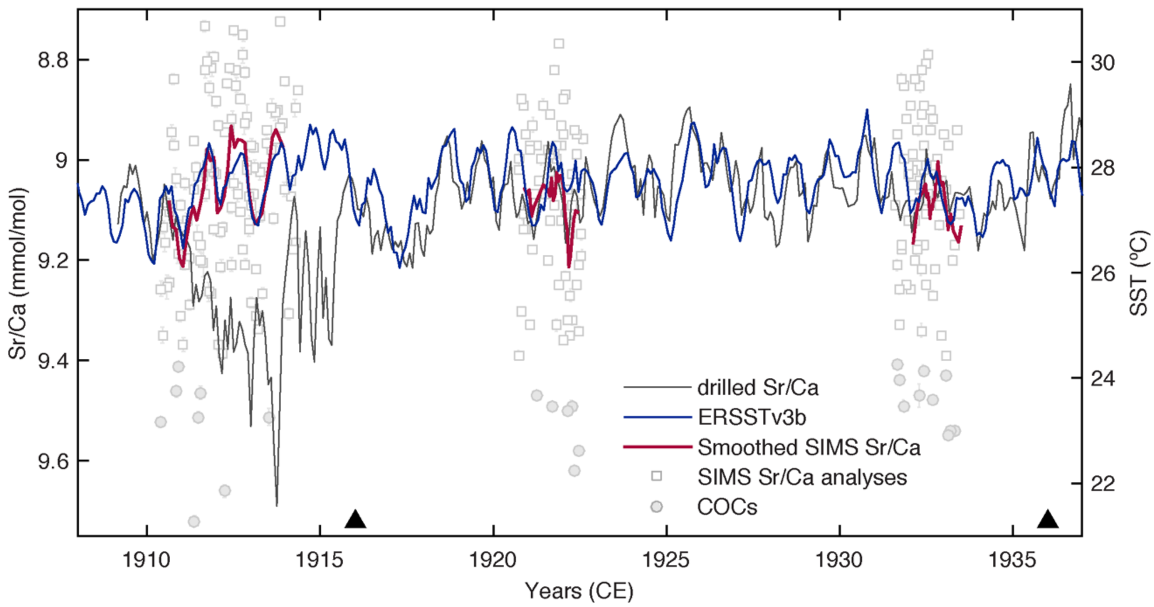

Figure 3-4: Conventional ICP-OES Sr/Ca (grey line) from core NB9 plotted against ERSSTv3b (blue line) and smoothed SIMS Sr/Ca (red line). Squares represent individual SIMS analyses used to derive the smoothed SIMS Sr/Ca time series. Filled circles denote individual SIMS analyses that are removed prior to smoothing.

Smoothed Sr/Ca time series across 1931-1933 and 1920-1922 from NB9 generally follow both the conventional Sr/Ca record and ERSST, albeit with a few discrepancies. We employed a sampling resolution of ~400um for SIMS Sr/Ca measurements across both these intervals, which worked well for the modern corals with higher extension rates 16-18mm/yr, but was not ideal for samples from NB9, which has a somewhat slower extension rates of 10-14mm/yr. Without enough analyses/month, the smoothed SIMS Sr/Ca time series from do not perfectly reproduce SST variability across their respective intervals. However, the SIMS data from these sections confirm that any trace diagenesis present in the in 1918-1935 horizon of NB9 does not significantly impact drilled Sr/Ca measurements.

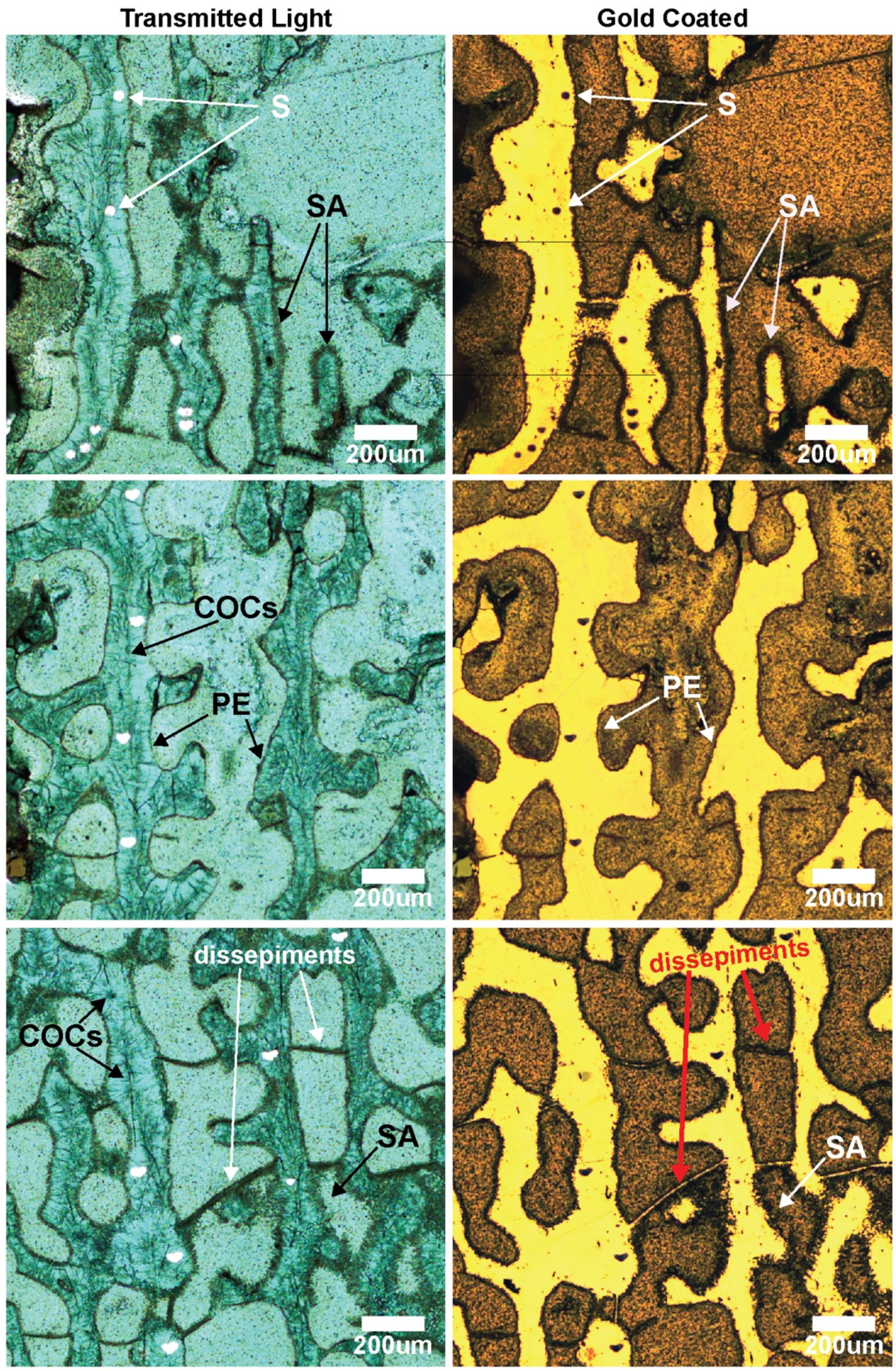

Figure 3-5: Transmitted (left) and reflected (right) images of thin sections from the 1911-1914 horizon of NB9. SIMS analyses (S) are shown as white spots in the transmitted light images and black spots in the reflected light images. Top and bottom panels show varying degrees of secondary aragonite infilling (SA), while panels in the middle show well preserved edges (PE).

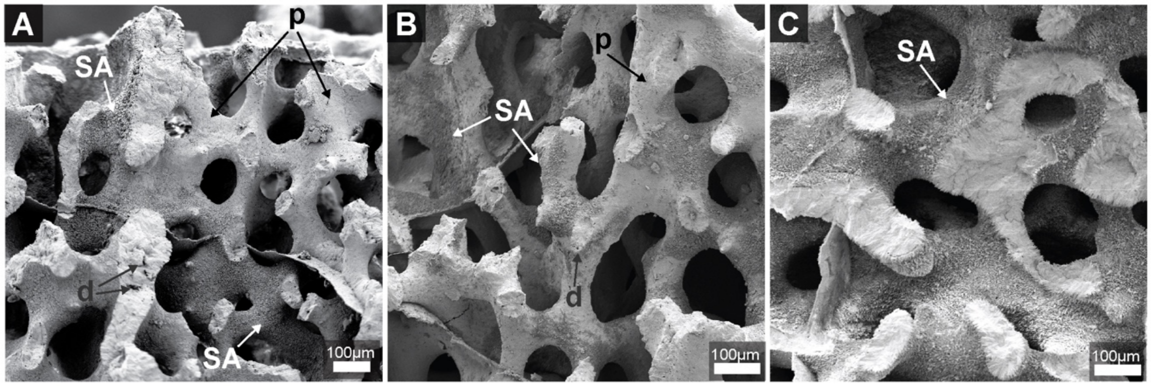

Figure 3-6: Representative SEM images of preservation in fossil coral NB9. Between 1931-1935 (A) and 1920-1922 (B), the coral skeleton is mostly well preserved (p), with a few patches of secondary aragonite (SA) and very minor dissolution (d). Between 1911-1914 (C), the coral skeleton is more consistently covered in secondary aragonite crystals.

Thin sections from the 1911-1914 horizon of NB9 show varying degrees of secondary aragonite infilling (Figure 3-5), which were likely sampled when generating the drilled Sr/Ca record. For SIMS Sr/Ca analyses from this horizon, we accounted for the slower extension rate of NB9, and sampled 3-4 spots between consecutive dissepiments, a skeletal feature that is deposited ~monthly [e.g. *DeCarlo and Cohen*, 2017], rather than sampling every 400μm. Between 1911-1914, the drilled Sr/Ca record yields an average value of 9.27±0.02mmol/mol (n=46), equivalent to an artificial cooling of ~3˚C. SIMS analyses across this same interval yields an average Sr/Ca value of 9.06±0.02mmol/mol, which is more consistent with drilled Sr/Ca from the rest of NB9. Smoothed SIMS Sr/Ca across this horizon reproduce seasonal cycles observed in SST (Figure 3-4).

3.5 Discussion

3.5.1 Reproducibility of SIMS analyses in modern corals

SIMS has been previously used to derive more accurate bulk estimates of Sr/Ca from altered fossil corals [*Cohen and Hart*, 2004; *Allison*, 2005; *Sayani et al.*, 2011], however none of these studies have thoroughly benchmarked SIMS Sr/Ca measurements against SST. Here, we present over 450 individual SIMS analyses from overlapping modern corals which demonstrate that this technique not only provides reproducible estimates of coral Sr/Ca, but may also provide derive reproducible SST reconstructions. Using only 3-4 SIMS analyses per month, we are able to reproduce bulk drilled Sr/Ca values within 0.3% in all three modern corals.

Our results also demonstrate that discrete SIMS analyses can be used to generate long and reliable records of monthly SST using as few as 3-4 analyses per month. The analytical precision of individual SIMS analyses from our earlier sessions was ±0.03 (1σ), three times worse than precision afforded by ICP-OES. During later sessions, better tuning of the beam and optics allowed for precisions similar to those of ICP-OES Sr/Ca measurements (±0.01; 1σ). Even with improved precisions, heterogeneity in skeletal geochemistry at μm-scales is far too large to derive meaningful temperature estimates from single SIMS analyses. A minimum of 15 SIMS analyses are needed to reproduce the Sr/Ca value of a single conventional measurement with 0.3%. Consistent with other studies [*Allison and Finch*, 2004; 2009], a 2-3month smoothing significantly reduces fine-scale heterogeneity in SIMS Sr/Ca measurements and isolates a Sr/Ca signal that is coherent with monthly-scale SST variability. With the exception of the SIMS transect from core

PM5, where we inadvertently measured multiple COCs, smoothed SIMS Sr/Ca time series three different modern coral transects are well correlated with SST (R=-0.5 to -0.8). As we very minimally tuned the age models for our SIMS measurements (up to 1-2 month for any given point), actual correlations between smoothed SIMS data and SST is likely higher.

Smoothed SIMS Sr/Ca measurements presented here have an average uncertainty of ±0.04mmol/mol (1σ), much larger than the ±0.01mmol/mol (1σ) obtained for ICP-OES Sr/Ca measurements. As we use a running mean filter to smooth the SIMS data, uncertainty is estimated using the standard error of all points used to calculate the mean at each time step. In addition to any errors in the Sr/Ca-SST calibration used, temperature estimates derived from smoothed SIMS data would have an additional uncertainty of ±0.6˚C (1σ). For studies needing to resolve much smaller changes in temperature, uncertainty in smoothed SIMS data can easily be reduced by simply increasing the number of analyses per month of coral growth. Here we used 3-4 analyses per month, however increasing this to ~20 analyses/month would theoretically yield uncertainties as low as ±0.022mmol/mol or ±0.3˚C, assuming that the SIMS points follow a Gaussian distribution about a true value that represents SST-related variability in coral Sr/Ca values.

3.5.2 Application of SIMS in altered fossil corals

Drilled Sr/Ca measurements from fossil coral NB9 are largely consistent with ERSST, yet during certain years, Sr/Ca-derived temperatures are up to ~1˚C cooler (Figure 3-4). SEM images do reveal the varying levels of secondary aragonite infilling, however we recognize that these SEM images may not be representative of the material actually sampled for Sr/Ca analyses. Targeted analyses of pristine coral material between 1920-

1922 in NB9, reproduce both the average Sr/Ca value of the drilled record, and more importantly the ~1˚C excursion in 1922. As such, it is likely that there is no diagenetic overprinting in this section of the drilled Sr/Ca record. Either the sparse network of observations in the 1920s used to calculate ERSST is not fully capturing temperature variability at our site [e.g. *Deser et al.*, 2010], or drilled Sr/Ca is recording is reflecting some other change in the coral's environment. The ultimate test for this targeted SIMS approach is extracting reliable Sr/Ca estimates from a heavily altered coral, such as the 1911-1917 section of NB9, where drilled Sr/Ca measurements erroneously predict temperatures that are up to 6˚C cooler than ERSST. Here, targeted analyses of pristine material allows us to completely bypass diagenesis and extract a bulk temperature estimate that is equivalent to average ERSST between 1911-1914 (27.7˚C vs 27.5±0.2˚C, respectively). Furthermore, by carefully making at least 3 measurements between dissepiments, instead of using a set spatial sampling resolution, we are able to produce a smoothed SIMS Sr/Ca time series that can be used to reconstruct SST.

3.6 Conclusion

Collectively, our results demonstrate that SIMS is a powerful tool that can be used to generate accurate, multi-year Sr/Ca time series from altered fossils. When compared to SIMS-based Sr/Ca profiles from modern corals that are calibrated to SST, fossil coral SIMS Sr/Ca time series represent the most accurate estimates of paleo-SST in fossil corals. As such, the present study serves as a "roadmap" for recovering accurate paleo-SST analyses from a wide variety of micro-scale analytical techniques, e.g. SIMS-based oxygen isotopes or laser ablation ICP-MS of proxies from a wide variety of marine carbonates.

However, given the sheer volume of analyses needed to overcome fine-scale heterogeneity in coral geochemistry (e.g. the 730 individual SIMS analyses presented here cost ~$15,000), microscale geochemical analyses are not practical in all circumstances. However, microscale analyses can and should be used to verify the accuracy of conventional, drilled Sr/Ca records from fossil corals, given that (i) no fossil coral is devoid of diagenesis, and (ii) even trace diagenesis can impart a significant artifact to coral Sr/Ca-based SST reconstructions, given the sensitivity of the coral Sr/Ca-SST relationship. As it stands, the vast majority of published fossil coral Sr/Ca-based paleo-SST reconstructions do not include SIMS Sr/Ca measurements, and as such it is likely that most of these reconstructions are compromised by diagenesis.

3.7 Acknowledgements

We would like to thank Nobumichi Shimizu, Peter Landry, Glenn Gaetani, and Kathy Rose from the Northeast National Ion Microprobe Facility for their assistance with operating and troubleshooting the ion probe used in this study. We'd also like to thank Yolande Berta and Georgia Tech's Center for Nanostructure Characterization for providing access to their SEM facilities.

APPENDIX A. SUPPLEMENTAL MATERIAL FOR "INTERCOLONY $\delta^{18}O$ AND SR/CA VARIABILITY AMONG CORALS AT PALMYRA ATOLL: TOWARDS ROBUST CORAL-BASED ESTIMATES OF MEAN CLIMATE CHANGE"

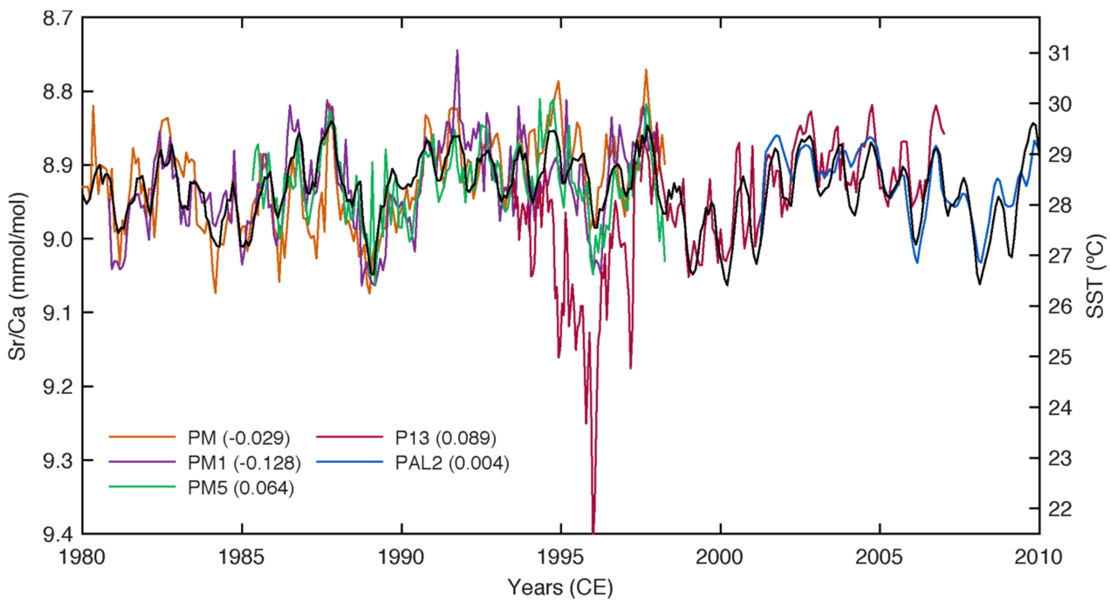

Figure A-1: Altered coral Sr/Ca in core P13 (red), compared to unaltered Sr/Ca records from cores PM (orange), PM1 (purple), PM5 (green), PAL2 (blue), and ERSST (black).

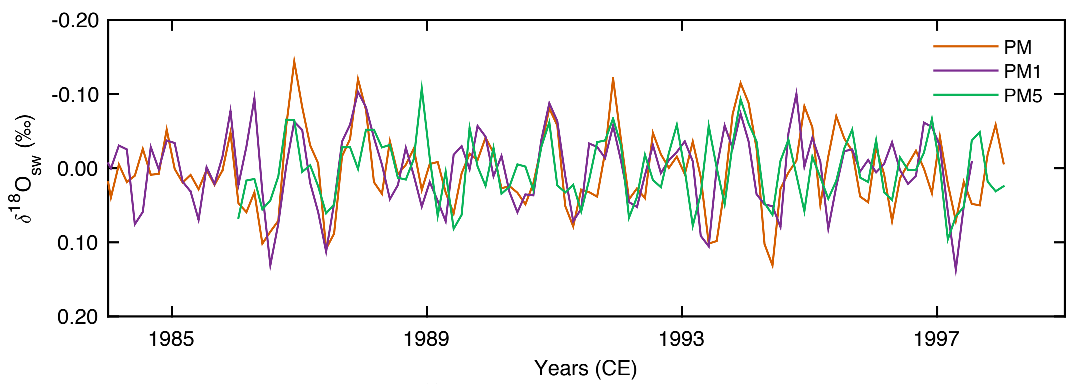

Figure A-2: Comparison of $\Delta\delta^{18}O_{sw}$ calculated for cores PM (orange), PM1 (purple),

and PM5 (green). These $\Delta\delta^{18}O_{sw}$ time series are integrated over time to derive the $\delta^{18}O_{sw}$ in Figure 2-6B.

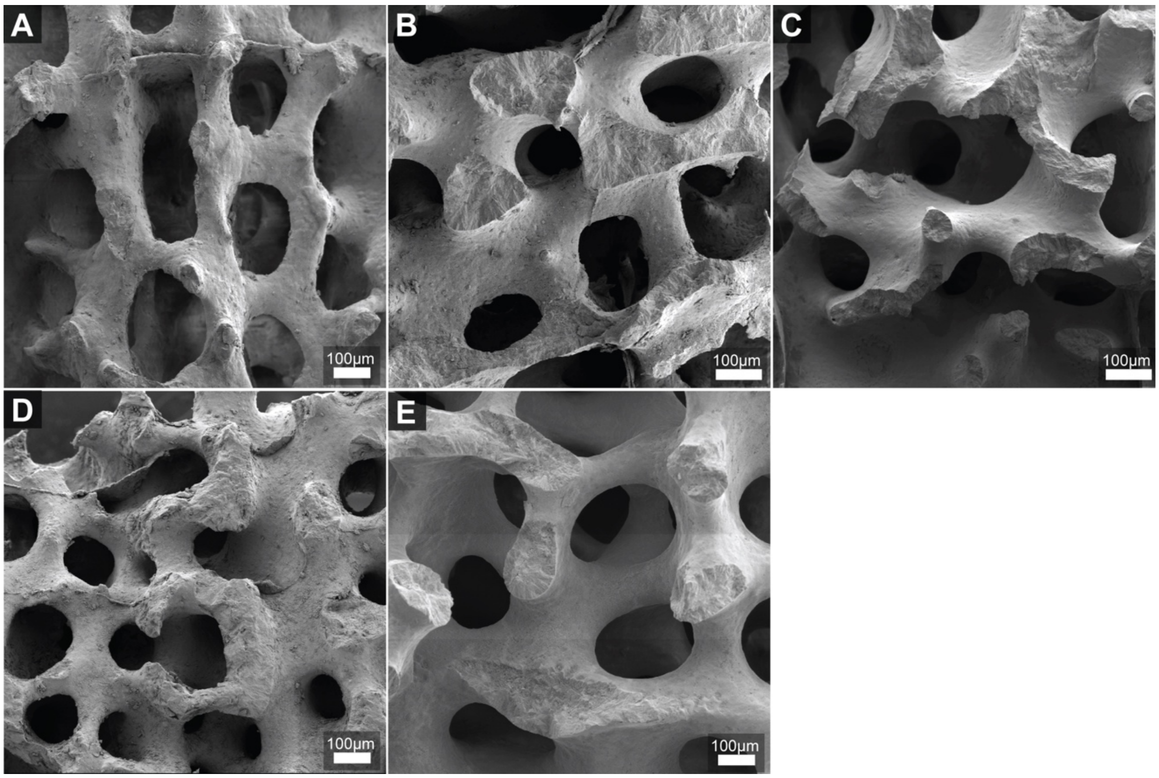

Figure A-3: Representative SEM images from cores PM (A), PM1 (B), PM5 (C), P13 (D) and PAL2 (F).

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